Dynamical Transition and Crystallization of Polymers

Koji Fukao* and Yoshihisa Miyamoto
Department of Fundamental Sciences, Faculty of Integrated Human Studies, Kyoto University, Kyoto 606-01 Japan

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The results of simultaneous time-resolved measurements of dielectric relaxation and x-ray scattering during isothermal crystallization from the glassy state of poly(ethylene terephthalate) are reported. We find a dynamical transition in the early stage of crystallization. The α-relaxation process, associated with glass transitions, is transformed into another relaxation process, the α' process, via a coexistence state before an observable change in x-ray scattering patterns due to the formation of crystalline structures appears. Analysis of x-ray scattering patterns reveals that this dynamical transition is related to a change in the thermal fluctuations of the electron density, i.e., to isothermal compressibility. [S0031-9007(97)04725-X]

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Crystallization, a first-order phase transition from a disordered liquid phase to an ordered solid phase, is a fascinating topic for which there exist many unsolved problems [1]. In particular, primary nucleation from a homogeneous state is the most fundamental process for the kinetics of crystallization. Nevertheless, few experimental studies with regard to the kinetics of the early stage of the ordering process have been reported because the rapid development of these processes in atomic systems makes such investigations technically very difficult.

In a polymer or colloid system, however, the characteristic time scale of dynamics is much slower than that for low-molecular weight materials [2]. For this reason, it is possible to investigate the kinetics of crystallization even in early stages for such large molecule systems. Recent studies have demonstrated that polymers and colloids are both suitable systems for investigation of the early stage of crystallization, where convenient real-time observations using several experimental techniques are available [3]. Scattering experiments reveal the existence of density fluctuations in the early stages of crystallization in polymers [4] and colloids [5]. Light scattering [6] and infrared absorption [7] show that in crystalline polymers a dynamical change begins before the crystalline structure is formed. However, the relation between dynamical change and structure formation is not yet clear, in particular with regard to the relation between dynamics in the amorphous phase and the formation of crystalline structure.

As a model system we chose a typical crystalline polymer, poly(ethylene terephthalate) (PET), because the crystal growth rate of PET is slow enough to allow for investigation of the real-time behavior during the crystallization process [8,9]. In this Letter, we report the results of simultaneous time-resolved measurements of dielectric relaxation and x-ray scattering during the isothermal crystallization process in order to investigate the relation between dynamics and structure formation, in particular, in the early stage of crystallization. Dielectric measurements reveal the presence of the α-relaxation process characterizing glass transitions, and x-ray scattering over a wide q range reveals the evolution of crystalline structure and higher-order structure. We found that a dynamical transition from the usual α process to another process, the α' process, occurs before the crystallization begins. This finding may provide a new prospect to explore the kinetics of primary nucleation.

The sample used in this study is poly(ethylene terephthalate) (RT580, $M_n = 5.9 \times 10^4$, $M_w/M_n = 2.51$), kindly supplied by Toyobo Co. Ltd. The glass transition temperature T_g of this material is approximately 75 °C. Amorphous films of PET were obtained by quenching into ice water after melting the samples at 290 °C for several minutes under an oil press. Gold was then deposited onto the film surfaces to serve as electrodes, except in the region through which x rays pass. The films were heated from room temperature to the crystallization temperature ($T_c = 97.5$ °C) in a vacuum chamber for measurements. After the temperature of the samples reached T_c, the f dependence of the complex dielectric constant and the q dependence of the x-ray intensity were simultaneously measured as a function of the crystallization time, where f and q are the frequency of the applied electric field and the scattering vector of scattered x rays, respectively. The dielectric measurements were made using an LCR meter (HP4284A) for the frequency range 20 Hz–1 MHz and an impedance analyzer (Solartron 1260) for 10^{-2}–100 Hz. The measurements were carried out at the High Intensity X-ray Laboratory at Kyoto University. The incident x rays used were point-collimated Ni-filtered Cu $K\alpha$ and Zr-filtered Mo $K\alpha$ from a fine-focus x-ray generator (RU1000C3, Rigaku Co. Ltd., Japan) [10]. Scattering intensities were measured using a two-dimensional position-sensitive detector. We used three different optical systems, each of which covers a different q range for x-ray scattering: $0.22 < q < 2.2$, $0.25 < q < 5.7$, and $0.69 < q < 17.5$ nm^{-1}. In each optical system, dielectric measurements were made simultaneously with x-ray scattering measurements. The data obtained using the three optical systems were connected to obtain scattering data over the wide q range $0.22 < q < 17.5$ nm^{-1}.

Figure 1 shows the time evolution of the imaginary part of the complex dielectric constant $\epsilon''(\omega)$ ($\omega = 2\pi f$) during the isothermal crystallization at $T_c = 97.5\,^\circ\mathrm{C}$. When the temperature reaches T_c, the peak of the α process is located at about 10^4 Hz, and the shape of the loss curve is asymmetric as normally seen in the α process of amorphous polymers [11]. In Fig. 1 we can see contributions from the dc conductivity on the lower frequency side and a tail of the β process, whose peak exists above 1 MHz. As time passes, the peak value of the α process decreases and another peak appears at 10–100 Hz. We refer to the process corresponding to this peak as the α' process. The shape of the dielectric loss curve of the α' process is quite different from that of the α process; the peak width is much broader than that of the α process, and the peak shape is symmetric. Shape parameters obtained by the Havriliak-Negami (HN) equation [12] are as follows: $\tilde{\alpha}_\alpha = 0.15$, $\tilde{\beta}_\alpha = 0.31$ at 0 min and $\tilde{\alpha}_{\alpha'} = 0.66$, $\tilde{\beta}_{\alpha'} = 1.0$ at 420 min. In order to extract the contributions from the α and α' processes, the dielectric loss is expressed as the sum of four contributions, the α-, α'-, and β-relaxation processes and the dc conduction in the following way:

$$\epsilon''(\omega) = \mathcal{T} \sum_{j=\alpha,\alpha',\beta} \frac{\Delta\epsilon_j}{[1 + (i\omega\tau_j)^{1-\tilde{\alpha}_j}]^{\tilde{\beta}_j}} + \frac{\tilde{\sigma}}{\omega^m}, \quad (1)$$

where $\Delta\epsilon_j$ is the dielectric strength of the j process, $\tilde{\alpha}_j$ and $\tilde{\beta}_j$ are shape parameters defined by the HN equation, τ_j is a relaxation time, and $\tilde{\sigma}$ and m are parameters determining the contributions from the dc electric conductivity due to impurities in polymers. Figure 2 exhibits the dielectric strength $\Delta\epsilon$ of both the α and α' processes, obtained by a nonlinear least-squares fit of $\epsilon''(\omega)$ to Eq. (1). The fit here was performed with the condition that the parameters for the β process are consistent with the values quoted in the literature [13]. We fixed these as $\tilde{\alpha}_\beta = 0.49$, $\tilde{\beta}_\beta = 1.0$, and $\tau_\beta = 6.3 \times 10^{-9}$ sec.

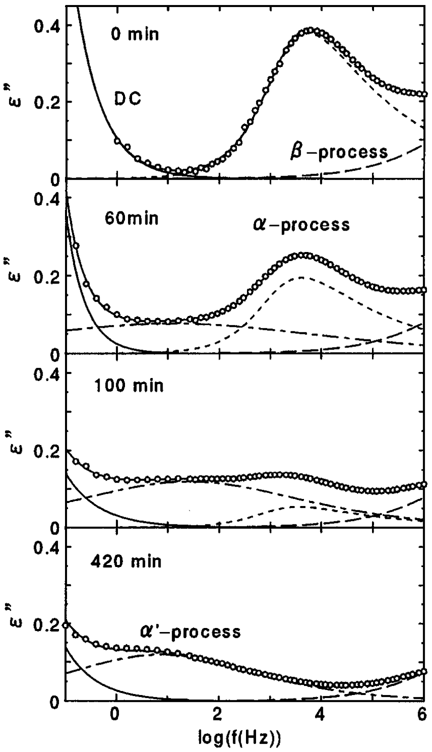

FIG. 1. Dependence of the dielectric loss on the logarithm of the frequency during the isothermal crystallization process (at 0, 60, 100, and 420 min). The open circles represent observed values, and the solid line overlapping with the open circles is given by a nonlinear least-squares fit to Eq. (1). The dotted line, dotted-broken line, and broken line are the contributions from the α process, α' process, and β process, respectively. The contribution on the lower frequency side is that from the dc conductivity due to impurities. This is represented by the solid line.

In Fig. 2, we see that $\Delta\epsilon$ of the α process decreases with time and then disappears, while $\Delta\epsilon$ of the α' process increases in the early stage and then decreases slowly. The characteristic time is estimated to be about 60 min for the decrease in the dielectric strength of the α process and the increase in the dielectric strength of the α' process. The sum of dielectric strengths of the α and α' processes ($\Delta\epsilon_{\alpha+\alpha'} \equiv \Delta\epsilon_\alpha + \Delta\epsilon_{\alpha'}$) is almost constant in the early stage of crystallization and then decreases with time. This suggests that two different dynamics, associated with the α and α' processes, coexist in the early stage; there is a *dynamical transition* where the dynamics of the amorphous phase change from those of the α process to those of the α' process via the coexistence state. After this stage we can see the gradual decrease in $\Delta\epsilon_{\alpha+\alpha'}$, which can be characterized by a time scale of 130 min. Therefore, we find two different changes in dielectric relaxation behavior during the isothermal crystallization

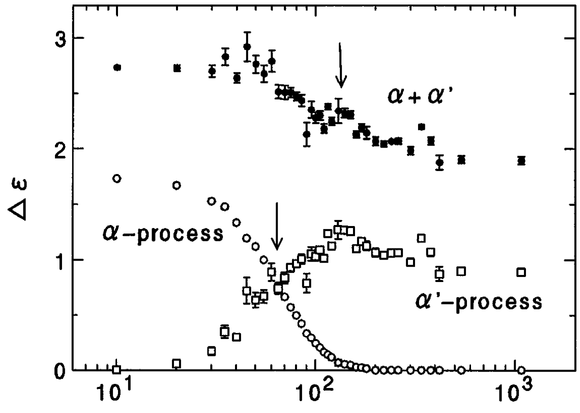

FIG. 2. Time evolution of the dielectric strength of the α process (○) and the α' process (□). The sum of dielectric strengths of the two processes is also plotted with the symbol ●. The values of $\Delta\epsilon_{\alpha+\alpha'}$ are shifted by 1.0 along the vertical axis to avoid overlapping with other symbols. The arrows indicate the two different characteristic times.

process. One of these is the change from the α-relaxation process to the α'-relaxation process, and the other is the decrease in the sum of the dielectric strengths of the α and α' processes.

What kind of structural change occurs while the abovementioned change is occurring in the dielectric relaxation process? Simultaneous x-ray scattering measurements can give an answer. We find two dominant regions within the q range observed in the present measurement, one a small-angle x-ray scattering region (SAXS, $0.2 < q < 2\ \mathrm{nm}^{-1}$) and the other a wide-angle x-ray scattering region (WAXS, $5 < q < 17.5\ \mathrm{nm}^{-1}$). The time evolution of the SAXS profile, Iq^2 vs q plot, shows that after a temperature jump from room temperature to T_c, a peak appears, and its intensity, $(Iq^2)_{\max}$, grows with time, where Iq^2 is the Lorentz factor-corrected intensity. The peak results from the periodicity in the lamellar structure which is usually observed in crystalline polymers. The peak position, $q_{\max}$, slightly shifts to larger values with time: $q_{\max} \sim 0.6\ \mathrm{nm}^{-1}$ at 10 min to $q_{\max} \sim 0.8\ \mathrm{nm}^{-1}$ at 300 min. This suggests that the period of the lamella decreases with time during the crystallization. At the initial stage of crystallization, the peak intensity increases slowly with time. Then the peak intensity increases rapidly with time up to about 300 min. The latter process can be attributed to the growth of spherulitic structure.

In the case of PET, Imai *et al.* observed the growth of a small peak in the SAXS pattern during the induction period for crystallization which is different from the peak due to the formation of lamellar structure [4]. However, no small SAXS peak such as that reported by Imai *et al.* was observed in our measurements within the experimental accuracy. This is also the case in SAXS measurements using synchrotron radiation [14]. The appearance of the peak may strongly depend on the nature of the initial glassy states or on the method of sample preparation.

Analysis of the scattering pattern in the WAXS region, which provides information on crystalline structure, reveals that at 0 min, only the amorphous halo is observed. As time increases, the intensity of the amorphous halo, I_a, decreases and Bragg reflections appear simultaneously. The time evolutions of these two processes obey the same dynamical law. Within the q range accessible in the present measurement, two sets of Bragg reflections could be observed; one is a peak consisting of $0\bar{1}1$ and 010 reflections, and the other a peak consisting of $\bar{1}11$ and $\bar{1}10$ reflections. Because of the low crystallization temperature the contributions from the two Bragg reflections overlap to form a single peak [15].

In order to compare the time variation in the values obtained in different measurements such as dielectric relaxations, SAXS and WAXS, we introduce the reduced intensity $\zeta(t)$ as follows:

$$\zeta(t) = \frac{X(t) - X(\infty)}{X(0) - X(\infty)}, \tag{2}$$

where $X(t)$ is the intensity in question at time t, $\zeta(t)$ is the reduced intensity of $X(t)$, $X(0)$ is the initial value of $X(t)$, and $X(\infty)$ is the final value of $X(t)$. In Fig. 3 we have plotted several intensities, that is, dielectric strengths of the α process $\Delta\epsilon_\alpha$, the sum of the dielectric strengths of the α process and the α' process $\Delta\epsilon_{\alpha+\alpha'}$, the peak intensity due to lamellar structure $(Iq^2)_{\max}$ obtained by SAXS, the intensity of the amorphous halo I_a, and the intensities of the Bragg reflections, I_{B1} and I_{B2}, obtained by WAXS. We can see that the intensities obtained by SAXS, WAXS, and $\Delta\epsilon_{\alpha+\alpha'}$ can be reduced to a master curve through $\zeta(t)$. The process described by the master curve is due to the crystallization process in which crystalline structure and higher-order structure—lamellar structure—are formed simultaneously. The formation of the crystalline structures leads to a decrease in the total amount of the amorphous phase. As a result, the sum of the dielectric strengths of the α and α' processes begins to decrease.

Comparing the time evolution of the master curve for crystallization with that of $\Delta\epsilon_\alpha$, we find a distinct difference between the two time evolutions: the characteristic time for the dynamical change in the dielectric strength of the α process, τ_{dyn}, is about 60 min, while the characteristic time for the crystallization process, τ_{cryst}, is 130 min. This suggests that a *dynamical transition* from the α process to the α' process occurs as a precursor to the usual crystallization process.

We now discuss the structural change related to the dynamical transition prior to the crystallization. Detailed analysis of x-ray scattering profiles over the wide q range from 0.2 to $17.5\ \mathrm{nm}^{-1}$ reveals that there are several contributions, from scattering due to crystalline structure, thermal density fluctuations, higher-order structure, and very long-range fluctuations [16]. Among these four contributions, the scattering intensity due to thermal

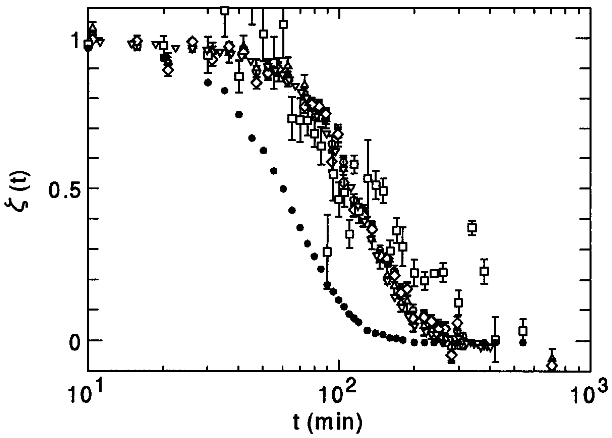

FIG. 3. Reduced intensity $\zeta(t)$ as a function of the logarithm of time for various intensities at 97.5 °C: •, $\Delta\epsilon_\alpha$; □, $\Delta\epsilon_{\alpha+\alpha'}$; ∘, I_a; △, I_{B1}; ◇, I_{B2}; ▽, $(Iq^2)_{\max}$. The values $X(0)$ and $X(\infty)$ for each measurement were chosen appropriately.

density fluctuations, I_f, changes with the occurrence of the dynamical transition. The intensity I_f is empirically expressed by the form $I_f(q) = A_R \exp(B_R q^2)$, where A_R and B_R are constants [17]. The prefactor A_R is equal to the structure factor of the forward scattering:

$$\begin{aligned} A_R &= \int d\mathbf{r} \langle \delta\rho(\mathbf{r}) \delta\rho(\mathbf{0}) \rangle \\ &= \rho^2 k_B T \kappa_T \propto \langle (\Delta N)^2 \rangle, \end{aligned} \tag{3}$$

where ρ is the electron density, $\delta\rho$ the electron density fluctuation from the average value, k_B the Boltzmann constant, T the temperature, κ_T the isothermal compressibility, and ΔN the fluctuation in electron number. The thermal density fluctuation, A_R, displays a maximum at approximately τ_{dyn} during the time evolution process, as shown in Fig. 4. Since the compressibility of the amorphous phase is usually larger than that of the crystalline phase, the term A_R is expected to decrease monotonically with a characteristic time τ_{cryst} in an ordinary ordering process, reflecting a decrease in the fraction of the amorphous phase. However, Fig. 4 shows that in the early stage of crystallization the intensity I_f due to thermal fluctuations initially increases with time, and then begins to decrease with time after reaching a maximum value. The time associated with the maximum is nearly equal to the characteristic time τ_{dyn} for the dynamical transition and differs from τ_{cryst}. This indicates that prior to the usual crystallization process there is a disordered state in which thermal fluctuation is enhanced, and via such an intermediate disordered state the amorphous phase with the α process changes into that with the α' process. After this dynamical transition the crystallization begins to produce normal crystalline and higher-order structure.

In summary, we made simultaneous time-resolved measurements of x-ray scattering and dielectric relaxation during the crystallization process in poly(ethylene terephthalate). We found the existence of a dynamical transition occurring prior to the beginning of normal crystallization. We hope that the present study will lead to a breakthrough in the investigation of primary processes of crystallization and stimulate development in this field.

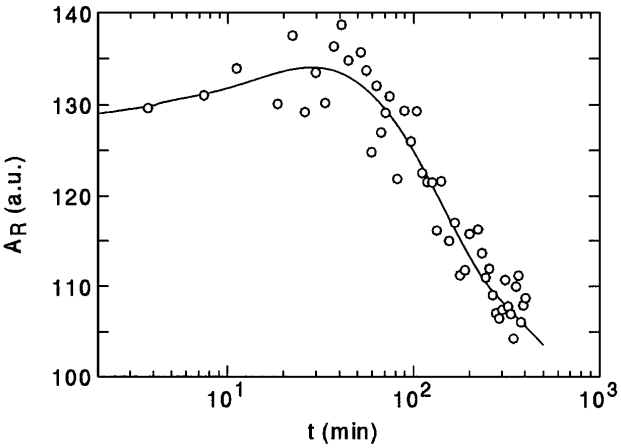

FIG. 4. Time dependence of the scattering intensity due to density fluctuations during the isothermal crystallization process at 97.5 °C. The solid line is to serve as a guide to the eye.

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*Electronic address: fukao@crystal.phys.h.kyoto-u.ac.jp

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