

Orientation Fluctuations of Poly(ethylene terephthalate) during the Induction Period of Crystallization

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The kinetics during the induction period of polymer crystallization is studied by means of depolarized light scattering measurements. The spinodal decomposition during this period is shown to be caused by orientation fluctuations of polymer segments. Time evolution of these orientation fluctuations can be described by the spinodal decomposition kinetics in terms of transformation from the isotropic to nematic phase proposed by Doi *et al.*

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Crystal nucleation is one of the phenomena showing typical first order phase transition. The general theory of crystal nucleation [1] is based on the assumption that the phase transformation is initiated by large-amplitude, localized fluctuations of some order parameter such as density leading to the appearance of small regions of the stable crystallizable phase. When these regions are larger than some critical size, they will grow and eventually crystallize. During the crystal nucleation process, time evolution of the number of crystal nuclei per unit volume N_V can be expressed by

$$N_V = I^S(t - t_0), \quad t \gg t_0, \quad (1)$$

where I^S is a steady-state nucleation rate, t is annealing time, and t_0 is an effective time lag, also described as an induction period. The induction period is defined as the time required to form the dense regions with a critical size from the homogeneous amorphous state. However, the time development in the ordering process and the cause for the ordering in the induction period have not yet been clarified, neither experimentally nor theoretically. Recently we [2,3] have investigated the structural formation of poly(ethylene terephthalate) (PET) in the induction period using wide-angle (WAXS) and small-angle (SAXS) x-ray scattering techniques and found that at a very early stage of the induction period the SAXS intensity begins to increase in the range of $0.2\text{--}0.5 \text{ nm}^{-1}$ in the length of the scattering vector q to become a clear peak with time. This peak is of course different from the well-known long period peak due to the alternation of crystalline and amorphous regions, which does not appear until the end of the induction period or the initiation of crystallization. It was also indicated that the time evolution of the intensity and the position of the new peak can be described by the kinetics of spinodal decomposition. These results suggest that the new SAXS peak is closely related to the crystal nucleation process. Therefore, the next step is to understand what the nature of the crystal nucleation or the induction period of crystallization is.

Flory [4] proposed the following two-step crystallization model: First cooperative ordering of the chains in a given region into a parallel alignment occurs without changing intermolecular interactions, and then longitudinal adjustment occurs, resulting in the more efficient packing of the chains in the parallel state to increase intermolecular interactions. The first stage of this process was studied using the lattice dynamics, showing that a parallel ordered state is more stable than a disordered one when the flexibility parameter of the polymer chain exceeds a specified critical value. It is noted that the first stage of Flory's model is very similar to the formation process of the nematic liquid crystalline phase. Doi and co-workers [5-8] have investigated the dynamics of the formation of the liquid crystalline phase of stiff polymers using a kinetics of two order parameters of concentration and orientation, and have shown the following kinetic equation:

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial \mathbf{r}} [D_{\parallel} \hat{\mathbf{u}} \hat{\mathbf{u}} + D_{\perp} (\mathbf{I} - \hat{\mathbf{u}} \hat{\mathbf{u}})] \left[\frac{\partial f}{\partial \mathbf{r}} + f \frac{\partial}{\partial \mathbf{r}} W \right] + D_r \mathcal{R}[\mathcal{R}f + f \mathcal{R}W]. \quad (2)$$

Here $f(\mathbf{r}, \hat{\mathbf{u}}, t)$ is the distribution function or the probability of finding a polymer parallel to the unit vector $\hat{\mathbf{u}}$ at time t and a position \mathbf{r} , \mathbf{I} is the unit tensor, W denotes the excluded volume type of potential between rods, D_{\parallel} and D_{\perp} are the translational diffusion constants parallel and perpendicular to the rod axis, respectively, D_r is the rotational diffusion constant, and \mathcal{R} is the rotational operator defined by $\mathbf{u} \times (\partial/\partial \mathbf{u})$. The orientation fluctuation $S_{\alpha\beta}$ in the α - β plane can be defined by

$$S_{\alpha\beta} = \int d\hat{\mathbf{u}} f_{\mathbf{q}}(\hat{\mathbf{u}}, t) (u_{\alpha} u_{\beta} - \frac{1}{3} \delta_{\alpha\beta}), \quad (3)$$

where $f_{\mathbf{q}}(\hat{\mathbf{u}}, t)$ is the Fourier component of $f(\mathbf{r}, \hat{\mathbf{u}}, t)$. When we assume that the polymer can move only along the chain axis, i.e., $D_{\perp} = D_r = 0$, orientation fluctuations are classified into three kinds of modes, so-called twist, bend, and splay. Of these modes the bend mode has the largest growth rate of fluctuation, and so the kinetic

equation for it is shown below for an example,

$$\frac{\partial S_{q \text{ bend}}}{\partial t} = -\frac{D_{\parallel}}{7L^2} \left[12 \left(1 - \frac{\nu}{\nu^*} \right) K^2 + \frac{25\nu}{9\nu^*} K^4 \right] S_{q \text{ bend}} \quad (4)$$

with

$$\mathbf{K} = \mathbf{q}L/2.$$

Here, ν is the concentration of rodlike segments and ν^* is the critical concentration at which the isotropic liquid becomes unstable:

$$\nu^* = \frac{16}{\pi d L^2}, \quad (5)$$

L and d being the length and the diameter of the rod, respectively. Equation (4) corresponds to the differential equation describing the spinodal decomposition given by Cahn [9]. Thus, when $\nu > \nu^*$, the isotropic system becomes unstable, and the fluctuation amplitude with a characteristic length grows exponentially with time. It is therefore expected that the exponential growth of the orientation fluctuations due to the parallel ordering of polymer segments can be observed experimentally. Such a result is the same as in the cases of the other two modes. Then we can observe the behavior of spinodal decomposition when the system satisfies the $\nu > \nu^*$ condition. These works are instructive when we interpret the time evolution of SAXS profiles observed during the induction period and the orientation fluctuations may play a very important role in the structure formation during the induction period. The purpose of this Letter is to confirm the role of the orientation fluctuations occurring in the induction period of crystallization by means of a depolarized light scattering technique.

Before going to the study of depolarized light scattering measurements we refer to the SAXS data in more detail to make clear the corresponding relation between the former and the latter experiments. In these works PET was employed because of the very slow crystallization rate and the high glass transition temperature $T_g = 348$ K, which makes it possible to fix the amorphous structure of the molten state by quenching to room temperature. Thus the time resolved measurements can easily be made. In order to obtain a sufficiently long induction period, annealing temperature was taken to be just above T_g . When annealed at 353 K, the induction period was about 100 min. Typical results from SAXS measurements are depicted in Fig. 1. Here the relative difference intensity, obtained by subtracting the intensity of the melt-quenched amorphous sample from those of annealed samples, is plotted against the magnitude of scattering vector q for different annealing times where $q = (4\pi/\lambda)\sin\theta$, λ is the wavelength of the radiation in the medium, and 2θ is the scattering angle. It is noted that in the early stage of the induction period, the scattering intensity profile shows

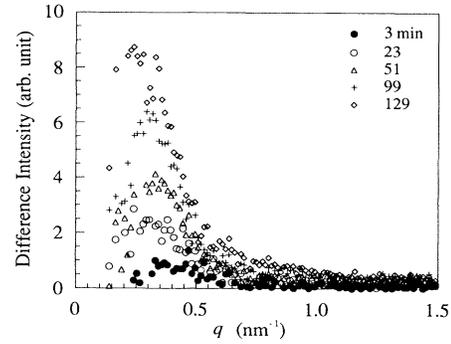


FIG. 1. SAXS profiles of PET films annealed at 353 K from the glassy state as a function of annealing time. The difference intensity means the observed intensity after subtraction of that for the melt-quenched sample.

a maximum and as the annealing time increases, the maximum position shifts toward smaller q while the maximum intensity increases. This indicates that the density fluctuations having a characteristic wavelength occur before formation of critical crystal nuclei because it was confirmed from the WAXS measurements [2] that no short range ordering is observed in the induction period. Surprisingly this growing process of density fluctuation is very similar to that of spinodal decomposition in phase separation.

In the following let us report the depolarized light scattering experiments. From an experimental point of view, the orientation fluctuations can be detected using the depolarized light scattering technique. For the analysis of the scattering from solids in which orientation fluctuations are randomly correlated, a statistical approach, developed by Stein and co-workers [10,11], was employed. The Rayleigh factor $R_{\perp}(q)$ for depolarized light scattering for such a system can be expressed by

$$R_{\perp}(q) = \left(\frac{\omega}{c} \right)^4 \frac{\langle \delta^2 \rangle}{15} \int_0^{\infty} g(r) \frac{\sin(qr)}{qr} (4\pi r^2) dr, \quad (6)$$

where q is the magnitude of the scattering vector, ω is the angular frequency of incident radiation, c is the velocity of light, $\langle \delta^2 \rangle$ is the mean-square anisotropy, and $g(r)$ is the function of orientation defined as $g(r) = (3\langle \cos\phi_{i,j} \rangle_r - 1)/2$, where $\phi_{i,j}$ is the angle between the optical axes of the i th and j th elements. The total integrated intensity or the invariant for contribution due to the orientation fluctuations I_{orient} can be expressed by

$$I_{\text{orient}} = \int_0^{\infty} R_{\perp}(q) q^2 dq = \frac{2\pi^2}{15} \left(\frac{\omega}{c} \right)^4 \langle \delta^2 \rangle. \quad (7)$$

Then we evaluate the orientation fluctuation using the invariant expressed by Eq. (7).

PET having number-averaged molecular weight $M_n = 25000$ and polydispersity $M_w/M_n = 2.5$ was supplied by Toyobo Co. Ltd. The PET sample was dried at 423 K for

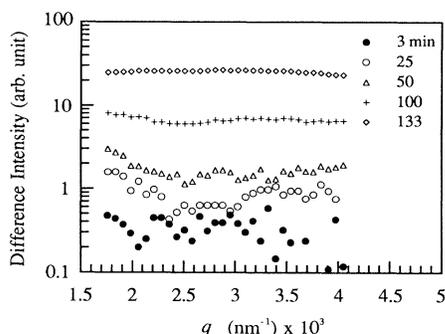


FIG. 2. Depolarized light scattering profiles of PET films annealed at 353 K from the glassy state as a function of annealing time.

240 min and melted at 563 K for 2 min. The melt sample was immediately quenched into ice water in order to obtain a completely amorphous PET sample in the glassy state. The isothermal annealing of the amorphous sample was performed on a hot stage (Linkam 600T) at 353 K. This annealing condition is the same as that of the SAXS measurements described above, so that the induction period of crystallization was about 100 min. The annealing process was followed by the time-resolved depolarized light scattering measurements. The sample was irradiated by a plane-polarized He-Ne laser beam ($\lambda = 633$ nm) on the hot stage and the scattered light intensity under depolarized conditions was recorded by a 38 photodiode array system.

Figure 2 shows the semilogarithmic expression of time evolution of the depolarized light scattering intensity in the early stage of the annealing process of the sample at 353 K as a function of q , from which the depolarized intensity of the unannealed sample was subtracted. During the induction period the scattering profiles are almost independent of q and the scattering intensity increases with annealing time. Figure 3 shows the time dependence of the invariant calculated by Eq. (7) in a semilogarithmic scale where the invariant for orientation fluctuations, I_{orient} , is normalized to that for a sufficiently annealed sample which was taken to be unity. As can be seen from the figure, the invariant appears to increase almost exponentially with annealing time until 50 min, but between 50 and 100 min, it levels off somewhat. After the induction period, the rate is suddenly accelerated and the invariant increases exponentially again, which is due to the formation of spherulite texture. The exponential increase of the invariant until 50 min agrees with the prediction of Doi's theory, suggesting that the parallel ordering actually occurs during the induction period. The two-step ordering process is also consistent with the SAXS results indicating early and late stages in the induction period.

In the following we discuss the critical concentration ν^* defined by Eq. (5). The PET molecule is composed of rigid terephthalate groups and soft ethylene groups; in other words, it consists of rigid rod segments connected

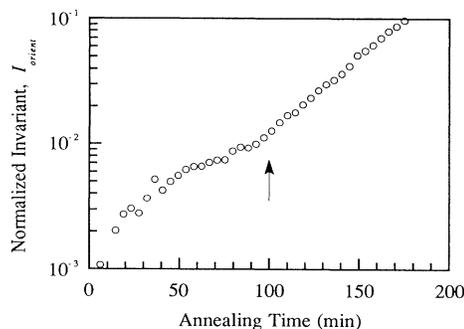


FIG. 3. Annealing time dependence of the invariant for the depolarized light scattering intensity of PET films. The invariant for orientation fluctuations, I_{orient} , is normalized to that for a sufficiently annealed sample which was taken to be unity. Arrow indicates the initiation time of crystallization.

by the flexible parts. The problem is whether or not such rod segments really satisfy Doi's criterion. In order to examine the criterion, we estimated the values of the length L and the diameter d of the rod in the amorphous state as follows. As an approximate value of L we adopted the persistence length in the wormlike chain model. Gonzalez *et al.* [12] reported that the persistence length of a PET molecule in the theta state is 1.2 nm. This value corresponds to the monomer unit length of 1.08 nm. For the cross-sectional diameter of the rod we took the van der Waals width of a benzene ring of 0.66 nm because it is considered that the benzene ring is freely rotating around the molecular axis just above the glass transition temperature [13]. If we use these values for the calculation, we get a critical concentration ν^* of 5.4 segments/nm³. The concentration ν of PET segments at a given temperature can be calculated from the density at that temperature and the mass of segment. Since the density of the glassy PET is 1.333 Mg/m³ and the mass of a monomer is 192 g/mol, the concentration of the segment in the glassy state is estimated to be 4.2 segments/nm³, resulting in $\nu < \nu^*$. In the glassy or melt state of PET we therefore cannot observe the orientation ordering or liquid crystalline state. When PET is annealed above the glass transition temperature, the internal rotation of ethylene groups begins to be allowed due to the release from the frozen state and the most stable chain conformation of the trans form is preferred to the gauche one. For example, in the case of *n*-butane [14] the trans conformation is about 3350 J/mol more stable than the gauche one. This conformational change increases the length of the rod segments. When the conformation of one of two CH₂ groups per monomer changes from gauche to trans as an average, it is expected that the rod length becomes 0.25 nm longer than that in the glassy state because one CH₂ repeating unit has a length of 0.25 nm. This increase of the rod length leads to the decrease of the critical concentration to a value of 3.7 segments/nm³. In this case, the condition $\nu > \nu^*$ is achieved

and the isotropic state becomes unstable. Then the phase transition from the isotropic to the orientationally ordered state occurs following the kinetics of spinodal decomposition. After such parallelization of the polymer chains in a given region, longitudinal adjustment occurs resulting in the more efficient packing of the parallel oriented chains to form a crystal nucleus.

Additional support for spinodal decomposition due to orientational fluctuations: Brochard-Wyart and de Gennes [15] indicated that even molten polymers show a spinodal decomposition when the chain orientation is temporarily given by a rapid stretching.

To summarize we have demonstrated by means of the depolarized light scattering technique that the kinetics during the induction period of PET is determined by the orientation fluctuations. The exponential growth of the orientation fluctuations in the induction period can be understood in terms of spinodal decomposition obeying Doi's theory.

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[1] K. F. Kelton, in *Solid State Physics*, edited by H. Ehren-

reich and D. Turnbull (Academic, New York, 1991), Vol. 45, p. 75.

- [2] M. Imai, K. Mori, T. Mizukami, K. Kaji, and T. Kanaya, *Polymer* **33**, 4451 (1992).
- [3] M. Imai, K. Mori, T. Mizukami, K. Kaji, and T. Kanaya, *Polymer* **33**, 4457 (1992).
- [4] P. J. Flory, *Proc. R. Soc. London A* **234**, 60 (1956).
- [5] T. Shimada, M. Doi, and K. Okano, *J. Chem. Phys.* **88**, 2815 (1988).
- [6] M. Doi, T. Shimada, and K. Okano, *J. Chem. Phys.* **88**, 4070 (1988).
- [7] T. Shimada, M. Doi, and K. Okano, *J. Chem. Phys.* **88**, 7181 (1988).
- [8] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).
- [9] J. W. Cahn, *J. Chem. Phys.* **42**, 93 (1965).
- [10] R. S. Stein and P. R. Wilson, *J. Appl. Phys.* **33**, 1914 (1962).
- [11] J. Koberstein, T. P. Russel, and R. S. Stein, *J. Polym. Sci. Polym. Phys. Ed.* **17**, 1719 (1979).
- [12] C. González, F. Zamora, G. M. Guzmán, and L. M. Química-Física, *J. Macromol. Sci. Phys. B* **26**, 257 (1987).
- [13] R. Gehrke, M. Gulibrzuch, A. Klaue, and H. G. Zachmann, *A.C.S. Polym. Prepr.* **29**, 64 (1988).
- [14] H. Tadokoro, *Structure of Crystalline Polymers* (Wiley, New York, 1978).
- [15] F. Brochard-Wyart and P. G. de Gennes, *C.R. Acad. Sci. Paris* **306** (II), 699 (1988).