

Crystal Nucleation in Polymer Glasses

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A new finding is reported that the structure formation in the induction period of polymer crystallization involves a spinodal decomposition type of phase separation. This has been revealed for poly(ethylene terephthalate) using a small angle X-ray scattering technique when it was crystallized just above the glass transition temperature T_g from a melt-quenched glass. Further, the depolarized light scattering experiments have clarified that the cause for such phase separation is the local ordering due to parallel orientation of polymer segments before crystallization.

Keywords: Polymer crystallization/ Induction period/ Spinodal decomposition/ Small-angle X-ray scattering/ Depolarized light scattering

A great number of studies have been reported concerning the polymer crystallization, but the mechanism of crystal nucleation, which is one of the most important unsolved problems, has hardly been investigated probably because of the difficulty in finding a clue to solve it. In recent years we have been studying what happens during the induction period before the start of crystallization using a small-angle X-ray scattering (SAXS) and a depolarized light scattering (DPLS) techniques [1-4]. We first found that during the induction period a new SAXS peak appears at a very early stage and grows with time when poly(ethylene terephthalate) (PET) was crystallized from the glassy state just above the glass transition temperature T_g . In this report we will show the importance of this new peak as a clue to understand the nucleation in polymer crystallization.

When a melt-quenched amorphous PET sample was crystallized at 80°C, 5°C above $T_g=75^\circ\text{C}$, the induction period was about 120 min. During this induction period the macroscopic density of the sample did not change and no exotherm was observed, while after the start of

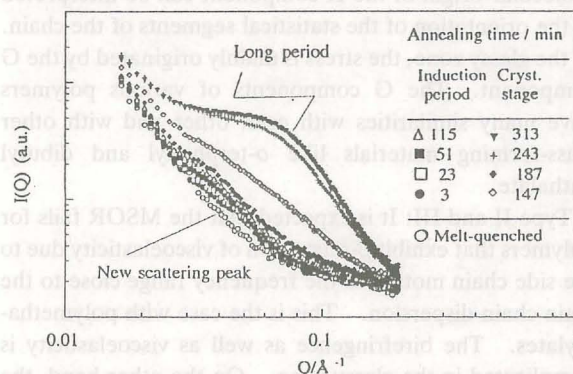


Figure 1. SAXS profiles of PET annealed at 80°C.

crystallization both the density and the isotherm increase rapidly. It was actually confirmed from wide-angle X-ray scattering experiments that these abrupt changes correspond to crystallization. Figure 1 shows the time-resolved SAXS profiles as a function of the length of scattering vector Q in the logarithmic expression. The scattering curve for the melt-quenched sample decreases monotonously with Q . Once the sample is annealed, a

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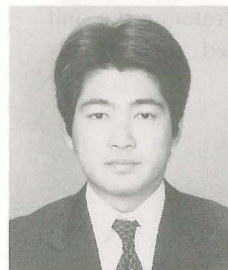
The structure and molecular motion of polymer substances are studied mainly using scattering methods such as neutron, X-ray and light with the intention of solving fundamentally important problems in polymer science. The main projects are: the dynamics in disordered polymer materials including low-energy excitation or excess heat capacity at low temperatures, glass transition and local segmental motions; the mechanism of structural development in crystalline polymers from the glassy or molten state to spherulites; formation processes and structure of polymer gels; the structure and molecular motion of polyelectrolyte solutions; the structure of polymer liquid crystals.



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maximum begins to appear at around $Q=0.04 \text{ \AA}^{-1}$ and increases in intensity with time. After crystallization this new peak is covered with a well-known long period peak at around $Q=0.07 \text{ \AA}^{-1}$, which is due to the alternation of crystalline and amorphous regions. The scattering intensities of the annealed samples from which that of the quenched sample was subtracted are shown in the linear scale in Figure 2. When the scattering intensity at

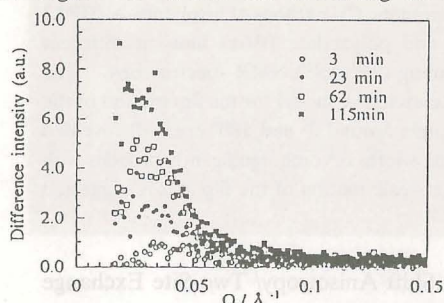


Figure 2. Difference SAXS profiles for the induction period after subtraction of that of the melt-quenched sample.

various Q s was plotted against the annealing time t , two stages were distinguished for each Q . In the early stage until about 20 min the intensity increased exponentially with the time, while in the late stage from 20 to 120 min the increasing rate of intensity considerably slowed down. These two stages are also observed in the time dependence of the peak position Q_m and the peak intensity I_m as shown in Figure 3. In the early stage Q_m

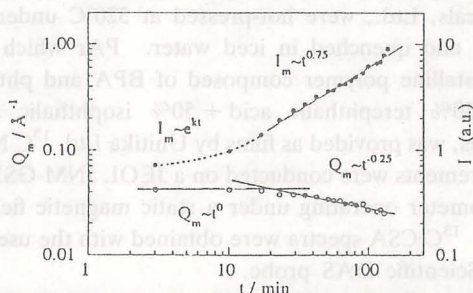


Figure 3. Annealing time dependence of Q_m and I_m .

does not change with the time while I_m increases exponentially. In the late stage the following experimental relations are obtained.

$$Q_m(t) \sim t^{-0.25}, \quad I_m(t) \sim t^{0.75} \quad (1)$$

These features agree well with the scattering behavior in the spinodal decomposition type of phase separation. Thus, the early and late stages can be described in terms of Cahn's linearized theory and Furukawa's scaling theory, respectively. According to the Cahn's theory, the density fluctuations with a constant wavelength increase in intensity with time, resulting that the scattering intensity $I(Q)$ increases exponentially with time and its peak position does not change. These predictions agree with the above-described experimental results. Furukawa's theory describes that for the late stage the amplitude of density fluctuations reaches the equilibrium value and the characteristic size $R(t)$ of a system grows through the diffusion and reactions of the clusters in the system, keeping a self-similarity. For the three-dimensional system ($d=3$) the time evolution of the intensity function in the late stage then becomes

$$I(Q, t) \sim R^3(t)S(x) \sim Q_m^{-3}(t)S(x) \quad (2)$$

where $x=Q/Q_m(t)$ and $S(x)$ is a universal scaling function which is given by

$$S(x) = x^2 / (2 + x^6) \quad (3)$$

This theory assumes that the characteristic size changes following a power law $R(t) \sim t^d$. Then, Q_m and I_m are scaled as

$$Q_m(t) \sim t^{-a}, \quad I_m(t) \sim t^b \quad (4)$$

where $b=3a$ and so $b/a=d=3$. The relations of eq. (4) are fairly in agreement with the experimental results of eq. (1) where $a=0.25$ and $b=0.75$, supporting the above assumption of the power law. In addition the universal scaling function of eq. (3) is plotted in Figure 4 where the

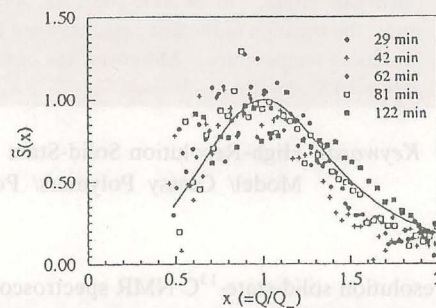


Figure 4. Observed universal scaling function $S(x)$.

function is normalized as $S(1)=1$. Independent of annealing time all the data in the late stage appear to be described by eq. (3). It can therefore be concluded that a kind of spinodal decomposition takes place during the induction period of crystallization. However, as the system investigated here consists of a single component, this conclusion further raises a new problem: what is the cause for such phase separation?

Doi *et al.* presented a kinetic theory of two order parameters, concentration and orientation, for the formation of the liquid crystalline phase of stiff polymers, predicting that the parallel orientation of stiff segments involves spinodal decomposition. In order to confirm this probability depolarized light scattering measurements were carried out. The total integrated intensity (invariant) I_{orient} due to orientation fluctuations increased exponentially in the early stage and then leveled off in the late stage. This shows that the parallel orientation of the segments actually occurs during the induction period.

The above experimental facts support the Flory's two-step crystallization model of cooperative ordering of the chains in a given region into a parallel alignment without changing intermolecular interactions and subsequent longitudinal adjustment to the more efficient packing of the chain in the parallel state. Our data also show that crystal nuclei do not appear until such local parallel ordering domains grow to a critical size, 85 Å in this case, which is considerably larger than the size of critical nuclei, 14 Å.

References

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