

Title	A New Discovery of Microphase Separation Initiating In the Induction Period of Polymer Crystallization : characteristic wavelengths at high temperatures (FUNDAMENTAL MATERIAL PROPERTIES-Polymer Materials Science)
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Citation	ICR annual report (1999), 5: 26-27
Issue Date	1999-03
URL	<a href="http://hdl.handle.net/2433/65195">http://hdl.handle.net/2433/65195</a>
Right	
Type	Article
Textversion	publisher

# A New Discovery of Microphase Separation Initiating In the Induction Period of Polymer Crystallization : characteristic wavelengths at high temperatures

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On the basis of the previous new discovery that a spinodal decomposition type of microphase separation occurs during the induction period for glass crystallization when a polymer is crystallized at low temperatures just above the glass transition temperature, the effect of crystallization temperature on the characteristic wavelength has been studied using poly(ethylene terephthalate) (PET) because this is an important factor for spinodal structures determining the whole skeleton of higher-order structure of crystalline polymers. For melt crystallization when PET is crystallized directly from the melt at high temperatures below the melting point, the characteristic wavelength is obtained to be a few micrometers which is two orders of magnitude larger than that for the glass crystallization. This may provide a possible elucidation for the large difference in size and density of spherulites between the glass and melt crystallization.

*Keywords* : Melt Crystallization / PET / Microphase Separation / Characteristic Wavelength

In previous papers [1] we reported a new discovery that a spinodal decomposition type of microphase separation is initiated in a very early stage of the induction period for glass-cold crystallization, ie when poly(ethylene terephthalate) (PET) is crystallized from the glass just above the glass transition temperature. This phenomenon is induced by orientational fluctuations or partial parallel orientation of rigid polymer segments when the average persistence length of the polymer molecules becomes larger than a critical value [2]. Such a mechanism is schematically shown in Figure 1. This is because the increase of the lengths of rigid segments causes the increase of their excluded volumes, making the system unstable, and the parallel orientation reduces their volumes. In the late stage of the spinodal decomposition the characteristic wavelength  $\Lambda_c$  grows with time, and when it attains a critical value the crystal

nucleation is initiated in the orientationally ordered regions. In polymer crystallization the characteristic wavelength is a very important factor since it is only a parameter characterizing the spinodal structure and considered to determine the whole skeleton of higher-order structure of crystalline polymers, so that it is interesting to investigate the temperature dependence of  $\Lambda_c$ . The observation of such a spinodal decomposition would, however, be possible only when the crystallization temperature is near either the glass transition temperature or the melting temperature, corresponding to a low segment mobility or a small supercooling depth, respectively, because a considerably long induction period is necessary to perform time evolution measurements.

In the present study the change of the characteristic wavelength has been investigated for melt-hot crystallization, ie when PET is crystallized directly

## 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.*



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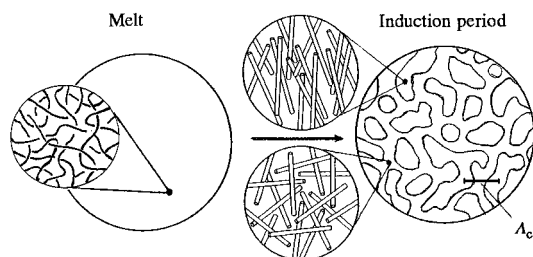
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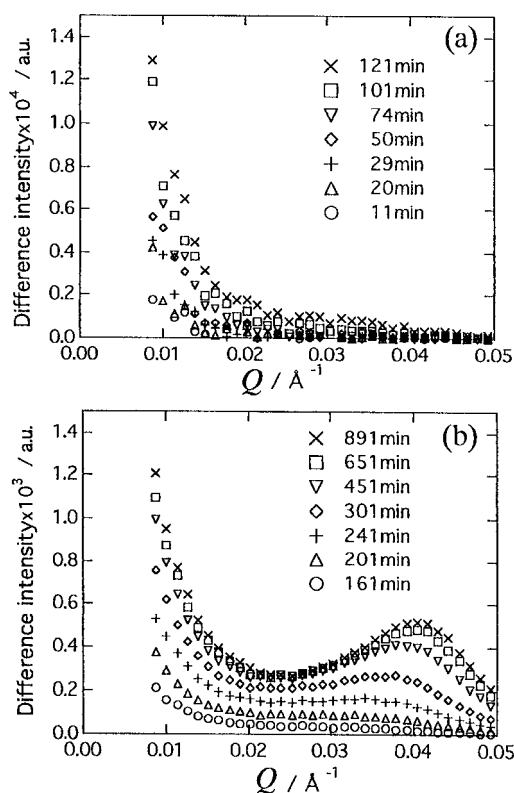
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**Figure 1.** Microphase separation induced by orientational fluctuations of rigid polymer segments before crystallization.

from the melt at high temperatures below the melting point. A PET sample with  $M_n=25,000$  and  $M_w/M_n=2.5$  was melted at  $290^\circ\text{C}$  ( $T_m=267^\circ\text{C}$ ) in the SAXS camera at the High-Intensity X-Ray Laboratory of Kyoto University, and SAXS measurements were carried out *in situ* when the sample was crystallized by jumping down to  $244^\circ\text{C}$  in this camera. The induction period was about 120min in this case. Figure 2 shows the time evolution of the difference intensity for this sample after subtraction of the scattering intensity from the melt sample at  $290^\circ\text{C}$ ; (a) and (b) correspond to the induction period and crystallization stage, respectively. As seen from Figure 2a, the intensity for  $Q < 0.02 \text{ \AA}^{-1}$  increases with time in the induction period, but no peak corresponding to the characteristic wavelength is observed. It may be considered that for the hot crystallization the characteristic wavelength is too large to be observed within a resolution of the used SAXS camera and the intensity at low  $Q$ 's is due to the contribution from the



**Figure 2.** Difference SAXS intensity curves of PET measured *in situ* as a function of crystallization time. Crystallized at  $244^\circ\text{C}$  from the melt.

tail of the peak of such a characteristic wavelength. As is clear from Figure 2b, even after crystallization it continues to increase with time, suggesting that the phase separation continues to grow without being interrupted by crystallization, which was also confirmed from polarized light microscopic observations. Further, after crystallization a well-known broad peak of long period due to the alternation of crystalline and amorphous layers starts to appear and increases in intensity with time. Here it should be noted that the peak position slightly shifts toward the higher  $Q$  with time. This phenomenon, which was first discovered by Zachmann et al [3], is clearly reconfirmed here where the separation from the strong low  $Q$  scattering is large enough to neglect the effect of overlapping. Zachmann et al tentatively explained such a strange result of the decrease of long period with time using a model that nascent crystalline lamellae having rough wavy surfaces come to have more and more smooth surfaces with annealing time, resulting in the decrease of long period. A more possible alternative elucidation by us is based on the distribution of lamellar thickness; the microphase separation produces two different regions, more-ordered and less-ordered in orientation and the former region first provides thicker lamellae and the latter region later thinner ones because of its higher density of entanglements. These thinner lamellae produced later decrease the observed average long period, shifting the scattering peak toward the higher  $Q$ .

In order to estimate the order of magnitude of characteristic wavelengths for the hot crystallization confocal scanning laser microscopic (CSLM) and polarized optical microscopic (POM) observations have been carried out. The former observation for the crystallization at  $220^\circ\text{C}$  indicated a spinodal pattern with  $\Lambda_c \approx 1 \mu\text{m}$  in the induction period [4]. If this value is true, the characteristic wavelengths for the hot crystallization would be two orders of magnitude larger than those for the cold crystallization. The POM observations showed a clear spinodal-like pattern after the beginning of crystallization; the dense and dilute domains of spherulites could clearly be distinguished and the interdomain spacings were estimated to be several tens  $\mu\text{m}$  at  $240^\circ\text{C}$  though they increased with crystallization time [5]. Such large difference in characteristic wavelength might give a possible explanation for a well-known great difference in number density of spherulites between both cases [6]; the two orders of magnitude in characteristic wavelength correspond to the six orders of magnitude in number density of spherulites.

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