



Crystallization through mesophase in poly(butylene terephthalate): Approach from dependence of growth rate on lamellar thickness



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ABSTRACT

The temperature dependence of the spherulitic growth rate of poly(butylene terephthalate) (PBT) has been investigated by optical microscopy and compared with the temperature dependence of the lamellar thickness. The changes in the dependence of the growth rate on the lamellar thickness are observed at three temperatures, 218, 208 and 157 °C. The middle temperature, 208 °C, corresponds to the temperature at which the temperature dependence of the lamellar thickness changes. The correspondence leads to the interpretation that the crystalline stem directly forms at the growth front above 208 °C and that the mesomorphic stem forms below 208 °C.

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1. Introduction

Poly(butylene terephthalate) (PBT) is a semi-crystalline polyester and widely used as an engineering plastic. PBT has two triclinic crystalline forms, α -form and β -form [1–7] and the smectic liquid crystal [8,9]. The α -crystalline structure is mainly obtained when PBT is crystallized from the melt or the glass. The β -crystalline structure forms by stretching the α -form and transforms reversibly to the α -form on removal of the strain. The smectic phase is obtained by stretching the glass below room temperature and transforms into the α -form by heating. The c -axis (fiber axis) length of the α -crystalline unit cell, ca. 11.6 Å is similar to that of the smectic periodicity, ca. 11.7 Å [8,9].

The morphology [10–12] and the growth rate [11,13–15] of the spherulite in PBT have been investigated for a long period. PBT has three types of spherulitic morphologies in the isothermal crystallization from the melt, usual, mixed and unusual types [10–12]. Di Lorenzo and Righetti have reported that the unusual type spherulite forms at the crystallization temperature $T_c = 193$ °C, the mixed type at $T_c = 204$ °C and the usual type at $T_c = 214$ °C and that the T_c -dependence of the spherulitic growth rate changes at 211 °C [11]. Yoshioka and coworkers also have confirmed that the usual type spherulite forms at 210 °C and the unusual type at 163 and 68 °C

[12]. In regard to the spherulitic growth rate, Di Lorenzo and Righetti have reported that the temperature dependence of the spherulitic growth rate changes at 211 °C and pointed that the temperature, 211 °C, is the regime II-III transition temperature by using the equilibrium melting temperature as 250 °C [11].

In a previous study [16,17], we found that the equilibrium melting temperature is 270 °C by the Gibbs-Thomson relation and that the T_c -dependence of the lamellar thickness l in PBT changes at a temperature $T_X = 208$ °C. According to the crystallization model through the mesophase [16–22], the results indicate that PBT crystallizes directly from the supercooled melt above $T_X = 208$ °C, while through the mesophase below T_X . Although the model also predicts the change in the T_c -dependence of the growth rate at T_X due to the difference of the crystallization processes [18,21,22], the research from the viewpoint of the comparison between the growth rate and lamellar thickness has not been performed in PBT.

The aims of this report are to obtain experimentally the T_c -dependence of the growth rate of spherulite in the wide temperature range in PBT by optical microscopy, to compare the T_c -dependence of the growth rate with that of the lamellar thickness, and to interpret the relation between the growth rate and the lamella thickness using the crystallization model through the mesophase.

2. Experimental section

The polymer used in this study was PBT with $M_v = 38,000$

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purchased from Sigma-Aldrich co. Ltd. The PBT pellet is sandwiched by cover glasses at 280 °C at a thickness of ca. 20 μm. The isothermal crystallization process at the crystallization temperature T_c between 120 and 220 °C after melting at 280 °C for 2 min was observed by a polarized or a bright-field optical microscope (Nikon ECLIPSE ME600) in order to measure the features and the sizes of the crystalline morphologies, respectively. For the observation of optical retardation, 530 nm sensitive color plate was inserted between the sample and the analyzer. The temperature of the sample were controlled by temperature-controller hot stages, Linkam THMS-600 and Linkam LK300 which give the cooling rates as 90 K/min and 300 K/sec, respectively. Linkam THMS-600 was mainly used for $T_c \geq 170$ °C and Linkam LK300, for $T_c \leq 170$ °C. In order to make immediately the temperature of the sample to be constant after cooling to T_c , the temperature-controlled sample stage in Linkam LK300 was covered with a copper cover plate.

3. Results and discussion

3.1. Temperature dependences of spherulitic growth rate and crystalline lamellar thickness

Fig. 1(a)–(d) show polarized optical micrographs taken with a sensitive color plate of the spherulites in PBT isothermally crystallized at $T_c = 197, 201, 214$ and 221 °C, respectively. The spherulites for $T_c = 197$ °C in Fig. 1(a) indicate that the Maltese cross is oriented at about 45° to the crossed polars and are categorized as the unusual type [10–12]. The morphology of the spherulites is of the unusual type at $T_c < 200$ °C (Fig. 1(a)) as reported by the other authors [10–12], but cannot be defined at $T_c > 200$ °C (Fig. 1(b)). The spherulites for $T_c = 221$ °C in Fig. 1(c) are axialites.

For $T_c > 210$ °C the boundaries of the spherulites are obscure in the polarized micrograph (Fig. 1(c) and (d)), but those in the bright-field micrographs are clearer (Fig. 1(e) and (f)). Fig. 2 shows the time-evolutions of diameters of spherulites or the maximum lengths of axialites, d , in PBT isothermally crystallized at several T_c from the melt; both of the spherulites and the axialites linearly grow with time. Fig. 3(a) and (c) show the T_c -dependence of the radial growth rate of spherulite or axialite, u , for PBT. The growth rate has a maximum at ca. 140 °C. The T_c -dependence of u obtained by Di Lorenzo [11] is also plotted in Fig. 3(a) and (c) and is similar to the present results.

In a previous study [17], we investigated the melting behavior of the lamellae in the heating process of the isothermally crystallized PBT by differential scanning calorimetry and small angle X-ray scattering (SAXS) measurement. The melting temperature of the crystalline lamella with thickness l_c mainly formed at T_c is determined. Fig. 3(b) shows the T_c -dependence of l_c . The broken curve in Fig. 3(b) represents the fitting one for the relation between l_c and T_c , which will be mentioned later in detail.

3.2. Analysis of the T_c -dependences of u compared with the l_c -dependence of u

In order to examine the T_c -dependence of u we consider the secondary nucleation process on the growth face of the crystalline lamella [23]. The growth rate of lamella depends on the size of the secondary critical nucleus and the secondary nucleus thickens by passing through the critical nucleus [24–26]. The growth rate of spherulite u is represented by

$$u = u_{0,i} \cdot \beta(T_c) \cdot \exp\left(-\frac{K_i}{T_c \Delta T_i}\right) \quad (1)$$

where $u_{0,i}$ is a prefactor, $\beta(T_c)$, the temperature dependent factor related to the diffusion constant, K_i , the nucleation constant related to the activation energy of the secondary nucleus, and ΔT_i , the degree of supercooling expressed by $\Delta T_i = T_i^0 - T_c$ using the equilibrium transition temperature between two phases, T_i^0 . The subscript index i refers to each phase transition between Liquid(L) and Crystal(C), and Liquid(L) and Mesophase(M), respectively: $i = LC$ and LM. The T_c -dependence of $\beta(T_c)$ is the Vogel-Fulcher type described by $\beta(T_c) = \exp[-d^* T_V (T_c - T_V)^{-1}]$, where d^* is the fragility index and T_V is the Vogel-Fulcher temperature. The values of d^* and T_V have been reported as 4.9 and 276 K, respectively, from the results of the dielectric measurement [27]. When the multiple secondary nuclei form on the substrate, which is categorized as regime II [28], K_i is defined as

$$K_i = \frac{2\sigma_{e,i}\sigma_{s,i}b_{0,i}T_i^0}{k_B\Delta H_i} \quad (2)$$

where $\sigma_{s,i}$ and $\sigma_{e,i}$ are the lateral and the folding surface energies between two phases, respectively, $b_{0,i}$, the thickness of the stem added on the substrate, k_B , the Boltzmann constant, and ΔH_i , the enthalpy difference between two phases. Since the length of the critical nucleus l_i^* equals to $2\sigma_{e,i}T_i^0/\Delta T_i\Delta H_i$, Eq. (1) is rewritten as

$$u = u_{0,i} \cdot \beta(T_c) \cdot \exp\left(-\frac{\sigma_{s,i}b_{0,i}l_i^*}{k_B T_c}\right). \quad (3)$$

The growth rate u of the normal L-C transition is given by Eqs. (1) and (2) with $i = LC$. Since the lamella with l_{LC}^* melts at T_c , the crystalline lamellar thickness l_c formed at T_c requires the excess length δl to thermodynamically stabilize the crystal: $l_c = l_{LC}^* + \delta l_{LC}$. Equation (3) can be replaced by

$$u = u_{0,LC} \cdot \beta(T_c) \cdot \exp\left(\frac{\sigma_s b_{0,LC} \delta l_{LC}}{k_B T_c}\right) \cdot \exp\left(-\frac{\sigma_{s,LC} b_{0,LC} l_c}{k_B T_c}\right). \quad (4)$$

The T_c -dependences of u and l_c in Fig. 3 gives the relation between u and l_c using Eq. (4). The relation between $u\beta^{-1}$ and $l_c T_c^{-1}$ in a semi-logarithmic scale is shown in Fig. 4. The relation changes at 218 and 208 °C. The relations between 208 and 218 °C and above 218 °C are linear, but the plot deviates from the linear relation below 208 °C. Since it has been predicted that the folded chain crystal has the constant δl [24,26] and $\delta l \ll l$, the linear relations above 208 °C in Fig. 4 indicate that the critical crystalline stems of thickness l_{LC}^* nucleate on the substrate. On the other hands, the relation below 208 °C cannot be explained by the growth mechanism same as that above 208 °C.

In order to clarify the origin of the changes at 218 and 208 °C in Fig. 4, the T_c -dependence of u is examined using Eqs. (1) and (2). T_{LC}^0 has been estimated as 270 °C by the Gibbs-Thomson relation from the SAXS results [16,17]. Fig. 5(a) shows $u\beta^{-1}$ against $[T_c(T_{LC}^0 - T_c)]^{-1}$ in a semi-logarithmic scale. The plot above 208 °C also shows two linear relations. Thus the growth rate for $T_c > 208$ °C has been fitted using two fitting parameters, $u_{0,LC}$ and K_{LC} . The non-linear regression method gives $u_{0,LC}^{(1)} = 5.63 \times 10^{12}$ μm/s and $K_{LC}^{(1)} = 7.44 \times 10^5$ K² for $T_c > 218$ °C, and $u_{0,LC}^{(2)} = 2.55 \times 10^7$ μm/s and $K_{LC}^{(2)} = 4.26 \times 10^5$ K² for 208 °C $< T_c < 218$ °C. The change at 218 °C can be explained as regime I-II transition when $K_{LC}^{(1)}/K_{LC}^{(2)} = 1.75$ is regard as 2 [23,29–32]. The spherulitic morphological change at regime I-II [29–32] has been reported, and the morphology of the spherulite also changes into the

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