Crystal Growth and Thermal Properties of Poly(trimethylene terephthalate)

○Daisuke Tadokoro, Takashi Konishi, Koji Fukao, and Yoshihisa Miyamoto
([1]Grad. Sch. of Human and Environmental studies, Kyoto Univ.
[2]Dept. of Ritsumeikan Univ.)

[introduction]

Poly(trimethylene terephthalate)(PTT) belongs to the polyester family, also known as 3GT(that is, PTT has three methylene groups in the monomer). Both poly(ethylene terephthalate)(PET)(2GT) and poly(buthylene terephthalate)(PBT)(4GT) have been intensively studied, but there were less studies performed on PTT.

There are many investigations about polymer crystallization via mesophase in this two decades. It was known the Keller's study about a mesophase as a prominent study, and they made the Keller's model of mesophase through the consideration of the Gibbs-Thomson relationship [1].

Schultz et al. reported that at 120 ℃ (strain=300 %) a transitional phase of PTT other than the equilibrium crystal structure forms [2].

Cavallo et al. have studied that the mesophase-mediated crystallization of poly(buthlene-2,6-naphthalate)(PBN) and they have reported that at higher cooling rates (e.g 100 K/s) a two-stage route is observed but at any cooling rates below 40 K/s it is not observed by wide angle x-ray study WAXD and flash-DSC measurement. They showed the rate of formation from the mesophase of PBN are faster than from the melt from the DSC data [3].

Furushima et al. have studied on the multiple melting behavior of PTT with the flash-DSC (from 0.1 K/s to 60,000 K/s) [4].

We first drawed the Gibbs-Thomson relationship of PTT with small angle x-ray measurement SAXS and at second measured the growth rate of PTT in the way of fast cooling rates (about 100 K/s). From these two quantitative data we showed that there are the transition temperature of PTT.

[experimental]

PTT films with thickness in the range of 200 μm are prepared for SAXS/WAXD.

Synchrotron X-ray mesurements was carried out at BL40B2 of SPring-8(λ =0.9 Å, camera length=1500mm for SAXS).

The measurement of the growth rate are performed by using the polarized microscope (Nikon Eclipse ME600). A fast cooling rate was realized by the two hotstage temperature-jumped system; one hotstage set at 280 ℃ (at the melt) and another hotstage set at the crystallization temperature (from 195 ℃ to 225 ℃).

[results and discussions]

Fig. 1 shows the Gibbs-Thomson relationship of PTT, the dependence of lamellar thicknesses at the melting point on the melting temperature. We defined the melting temperature as the temperature just behind starting the recrystallization. To fix the melting temperature we compared between the data of DSC, invariant, the degree of crystallization, WAXD intensity peaks and the lamellar thicknesses. The lamellar thicknesses were calculated with the Strobl's method.

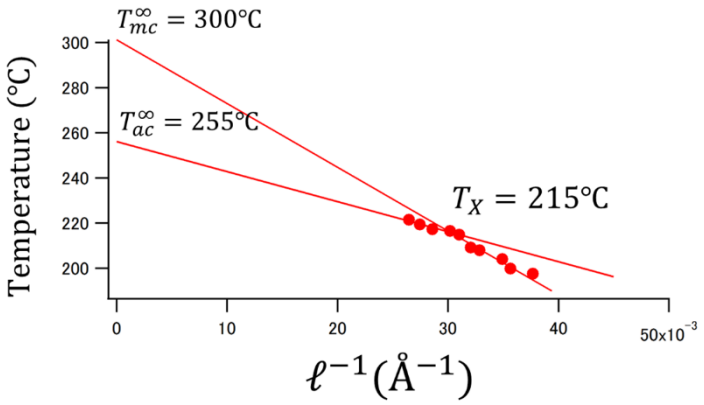

Figure 1

The Gibbs-Thomson equilibrium line of PTT.
The deviation from the equilibrium line at 215 ℃.
T_{ac}^{∞} is the equilibrium melting temperature of the melt-crystal transition.

Fig 1 depicts the deviation from the equilibrium line at 215 ℃, that is to say, we can draw two Gibbs-Thomson equilibrium lines; one means the equilibrium line of the phase transition between crystal and the melt and another means the line between crystal and the mesophase.

Fig.2 shows the temperature dependence of the growth rate, $\log(G/\beta)$ vs $1/T\Delta T$ (G: growth rate (μm/s), β: the vicious factor, T: crystallization temperature (℃), and ΔT: the supercooling, $\Delta T = T_{ac}^{\infty} - T$. T_{ac}^{∞} is the equilibrium melting temperature, T_{ac}^{∞} = 255 ℃). The deviation at 215 ℃ is also existed. This deviation might be caused by the superiority of mesophase (the probability of the the melt-mesophase nucleation is higher than the melt-crystal.).

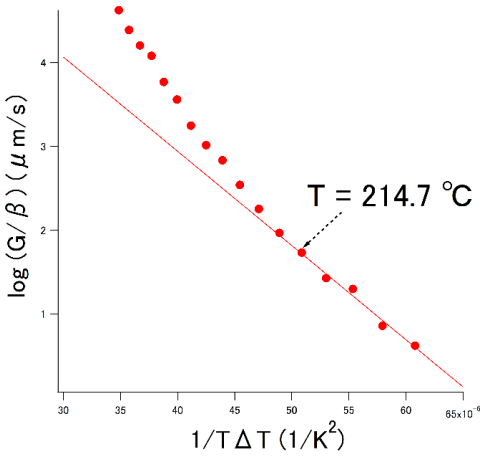

Figure 2

The temperature dependence of the growth rate, $\log(G/\beta)$ vs $1/T\Delta T$.
$\Delta T = T_{ac}^{\infty} - T$.

Fig.3 shows the two patterns of the temperature dependence of the growth rate, $\log(G/\beta)$ vs $1/T\Delta T$, that above 215 ℃ the equilibrium melting temperature is that of the melt-crystal transition ($\Delta T = T_{ac}^{\infty} - T$, T_{ac}^{∞} = 255 ℃), on the

other hand below 215 ℃ it is that of the melt-mesophase transition ($T_{am}^{\infty} =$ 240 ℃).
The equilibrium melting temperature of the melt-mesophase transition was calculated by the Gibbs-Thomson relationship and the empirical data of polyethylene [1].
The growth front of the lamellar growth must be the melt-mesophase transition.
K_A and K_B in Fig.3 are the slope of the temperature dependence of the growth rate, respectively K_A is the slope above 215 ℃, K_B is below 215 ℃. K_A and K_B equal $\sigma\sigma_e T_m^{\infty}/\Delta h$ (σ, σ_e: surface energy, Δh: heat of fusion).
In Keller's literature the deviate temperature of the Gibbs-Thomson equilibrium line requires the following eqution [1].

$$\frac{K_A}{T_{ac}^{\infty} - T_X} = \frac{K_B}{T_{am}^{\infty} - T_X} \qquad (1)$$

This equation implies at the transion temperature, T_X, the probability of the melt-crystal nucleation is equal to the melt-mesophase (and below T_X the melt-mesophase nucleation becomes predominant.).
The data of K_A and K_B in Fig.3 indicate a value of T_X of equation (1) close to a value of Fig.1. This is because the transition temperature of PTT is 215 ℃. But to get the high accuracy result we must perform the more accurate experiments for numerical analysis.

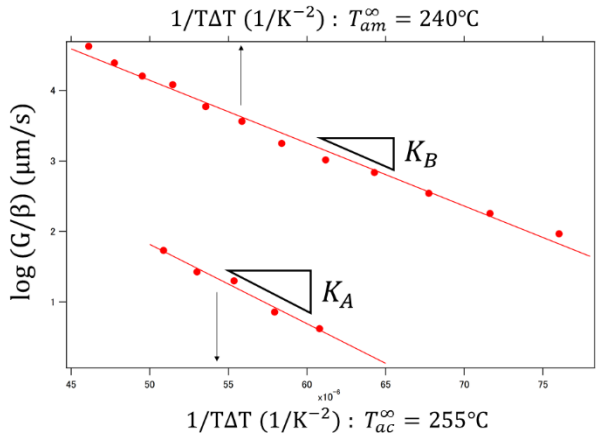

Figure 3

The two patterns of the temperature dependence of the growth rate, log(G/β) vs 1/TΔT above 215 ℃ the equilibrium melting temperature is that of the melt-crystal transition ($\Delta T = T_{ac}^{\infty} - T$, $T_{ac}^{\infty} =$ 255 ℃), below 215 ℃ it is that of the melt-mesophase transition ($T_{am}^{\infty} =$ 240 ℃).

[1]
Keller et al.,
J.Mater.Sci, 1994.
[2]
Schultz et al.,
Polymer, 2001.
[3]
Cavallo et al.,
Macromolecules, 2012.
[4]
Furushima et al.,
Euro.Poym., 2017.