

Crystallization and Melting Behavior of Poly(trimethylene 2,6-naphthalate)

정영규, 조원호, 이상철*

서울대학교 섬유고분자공학과, *금오공과대학교 고분자공학과

1. Introduction

Poly(trimethylene 2,6-naphthalate) (PTN) is a semicrystalline polymer whose preparation was first reported in 1969¹. As a new material, PTN has a potential for commercial use since 1,3-propanediol and 2,6-naphthalenedicarboxylic acid monomers recently become available in large-scale quantities. However, there has not been any report on its crystal structure, thermal property, mechanical property, and any other properties. It has recently proved in our previous report² that PTN has two crystal structures (α - and β -form) and that the temperature-induced crystal transition occurs between two crystal forms. As temperature is increased, α -form (pseudo-monoclinic) is transformed to β -form (triclinic), whereas the crystal transition from β -form to α -form does not occur. It is expected that PTN chain is stiffer than poly(trimethylene terephthalate) (PTT), since naphthalene ring in PTN is more rigid than benzene ring in PTT. Consequently, the PTN is expected to have higher glass transition temperature, higher melting temperature and better mechanical properties than those of PTT. PTN has higher glass transition temperature ($T_g = 76\text{ }^\circ\text{C}$) but lower melting temperature ($T_m = 207\text{ }^\circ\text{C}$) than those ($T_g = 45\text{ }^\circ\text{C}$, $T_m = 228\text{ }^\circ\text{C}$) of PTT, respectively, which is a peculiar thermal behavior. In the present study, we report the thermal behavior of PTN. Crystallization and melting behaviors for the samples subjected to various thermal treatments were thoroughly investigated using DSC, polarized optical microscopy and X-ray diffraction.

2. Experimental Section

PTN used in this study was synthesized by melt-condensation reaction of 1,3-propanediol with dimethyl-2,6-naphthalate using tetraisopropyl orthotitanate as a catalyst. All samples were carefully dried under vacuum. The intrinsic viscosity of PTN was 0.51 dl/g and its glass transition temperature and melting temperature were $76\text{ }^\circ\text{C}$ and $207\text{ }^\circ\text{C}$, respectively.

DSC measurement was performed on a Perkin-Elmer DSC-7 equipped with an intercooler system. Isothermal crystallization experiments were performed as the following procedure. The sample was heated under a nitrogen atmosphere to a temperature 30 °C higher than the melting peak temperature, held at the temperature for 3 min, and then quenched to the predetermined crystallization temperature, where they were held isothermally. Melting thermograms of the samples crystallized isothermally or dynamically were obtained under various heating and cooling rates.

The development of the spherulitic superstructure was monitored with an polarized optical microscopy (Nikon eclipse e600 POL) and the crystallization process recorded with a color video camera mounted on the microscope. The thin films were heated to 230 °C for 3 min on a hot stage to eliminate previous thermal history and then rapidly transferred to a Mettler hot stage (model FP-52) set at the desired crystallization temperature. The spherulitic growth rate was determined from the slope of the spherulite radius vs time plot. The spherulitic growth rate was reported by averaging three measurements.

The X-ray diffraction patterns were obtained with a MAC Science M18XHF X-ray diffractometer using Ni-filtered Cu-K α radiation ($\lambda=0.1542$ nm; 50 kV; 100 mA) at a scanning rate of 5 °/min. The samples for WAXD were prepared in powder and film forms.

3. Results & Discussion

The melting behavior of samples crystallized dynamically with various cooling rate was shown in Figure 1. Since the clear melting peak was observed at very slow cooling rate, it is tentatively concluded that PTN has a very slow crystallization rate. When the sample was annealed at 170 °C, the sample shows double melting peaks, as shown in Figure 2. This double melting peaks may arise from a melt/crystallization process, since the low-melting peak corresponding to the crystals formed at the annealing temperature become larger at the expense of the high melting peak as the scanning rate is increased. The high melting peak corresponds to the crystal recrystallized during heating in DSC. Figure 3 shows the Hoffman-Weeks plot to estimate equilibrium melting point (T_m^0) of PTN. A good linearity is obtained for PTN, where an extrapolation to the line $T_m = T_c$ yields $T_m^0 = 232$ °C.

Spherulitic growth was monitored at various crystallization temperatures from 135 to 200 °C. The spherulite radii measured from a series of video images taken at successive intervals were plotted versus time, as shown in Figure 4. Growth

rates were determined by from the slopes of a linear least-squares fit of the curves before impingement. Spherulitic growth rates measured for PTN are summarized in Figure 5. The maximum growth rate is observed at α . 160 °C, corresponding to an undercooling, $\Delta T \sim 70$ °C. At this temperature, the crystal transition between α - and β -forms occurs, as shown in Figure 6.

4. References

- 1) I. N. Duling and W. Chester, U.S. pat., 3,436,376 (1969)
- 2) Y. G. Jeong, W. H. Jo, and S. C. Lee, Proceedings of the Korean Textile Conference, 307, fall (1999)

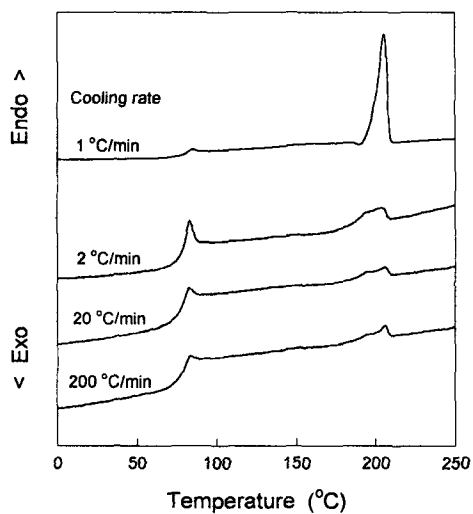


Figure 1. Melting thermograms for the samples crystallized dynamically at various cooling rate.

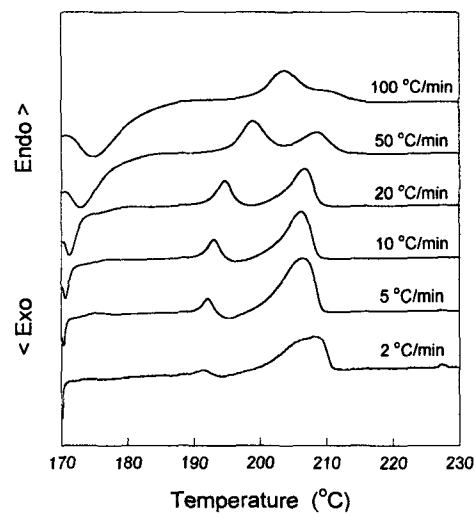


Figure 2. Melting thermograms with various heating rate for the samples crystallized isothermally at 170 °C for 1 hour.

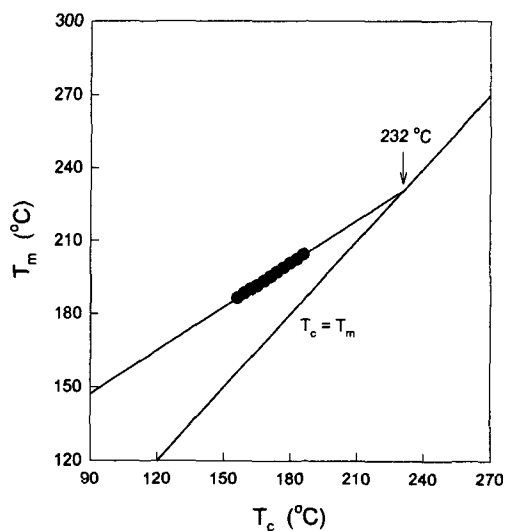


Figure 3. Hoffman-Weeks plot for PTN.

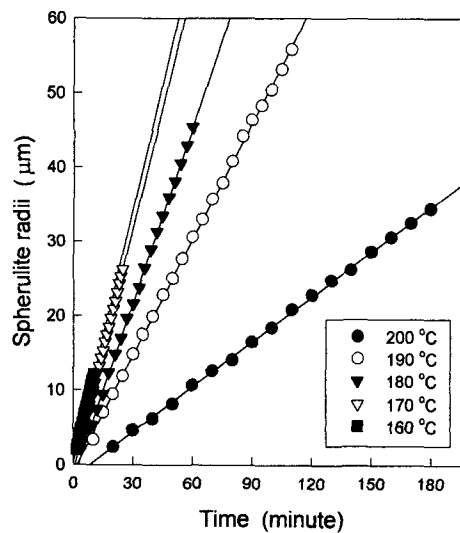


Figure 4. Spherulite radii vs time plots obtained from isothermal crystallization experiments.

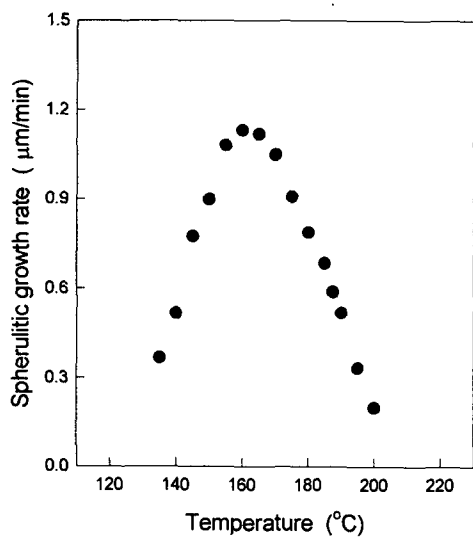


Figure 5. Spherulitic growth rates for PTN.

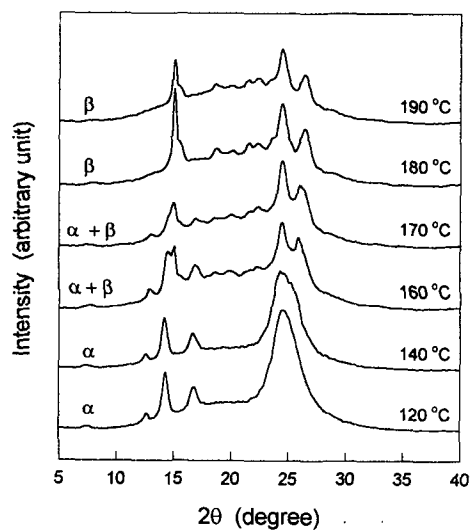


Figure 6. X-ray patterns for the samples crystallized isothermally.