

# Origin of High Melting Point of Substituted Poly(lactic acid) with Isopropyl Side Chains Revealed by Synchrotron WAXD/SAXS Simultaneous Measurements

Hironori MARUBAYASHI,<sup>1,\*</sup> Yuji HAMADA,<sup>2</sup> and Shuichi NOJIMA<sup>2</sup>

<sup>1</sup> Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,  
2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan

<sup>2</sup> School of Materials and Chemical Technology, Tokyo Institute of Technology,  
2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

## 1 Introduction

Recently, the side-chain-substituted poly(lactic acid)s (SPLAs) [1,2] have attracted attention as novel bioplastics to overcome weakness of poly(L-lactic acid) (PLLA), a representative bioplastic. However, their possibility as crystalline plastics still remains unexplored. We reported that the crystalline SPLA with isopropyl side chains [P(L-2H3MB)] had much higher melting temperature ( $T_m$ ) and crystallization rate as compared to PLLA, from which a great potential as high-performance bioplastics was demonstrated [1]. In this study, we investigated the non-isothermal crystallization process of P(L-2H3MB) by time-resolved (TR) WAXD/SAXS simultaneous measurements. We discuss the origin of high  $T_m$  of P(L-2H3MB) based on TR-WAXD/SAXS and thermal analysis.

## 2 Experiment

P(L-2H3MB) with  $M_n = 1.4 \times 10^5$  g/mol and  $M_w/M_n = 1.4$  was synthesized from L-valine [1].

TR-WAXD/SAXS simultaneous measurements were performed at KEK PF BL-6A ( $\lambda = 0.1500$  nm) using an FP84HT TA Microscopy Cell (METTLER TOLEDO) for cooling from 240 to 30 °C at 5 °C/min, during which data acquisition and interval times were set to 5 and 1 s, respectively. The temperature of samples packed in a washer was monitored by a resistance temperature detector.

Differential scanning calorimetry (DSC) measurements were conducted in lab using a power-compensated DSC (Diamond DSC, PerkinElmer Inc.) in the non-isothermal condition with the same temperature range (240 to 30 °C) and cooling rate (5 °C/min) as TR-WAXD/SAXS.

## 3 Results and Discussion

Fig. 1 shows TR-WAXD profiles during the cooling process from the melt for P(L-2H3MB). The crystallization of P(L-2H3MB) started (appearance of diffraction peaks) around 185 °C and the degree of crystallinity ( $X_c$ ) increased (increases in peak areas) with decreasing temperature. The crystal modification ( $\beta$ -form) was not changed during the non-isothermal crystallization. Note that shifts of peaks to higher  $2\theta$  (shorter spacing) with decreasing temperature would be attributed to thermal shrinkage of samples. The temperature dependence of  $X_c$  was obtained from TR-WAXD profiles. The peak temperature in  $dX_c/dT$  is 180 °C, which agrees with that in the DSC cooling curve. The equilibrium crystallization enthalpy ( $\Delta H_c^\circ$ ) was evaluated from the linear relationship

between  $X_c$  and the corresponding crystallization enthalpy ( $\Delta H_c^\circ$ ). The obtained  $\Delta H_c^\circ$  was converted to the equilibrium melting enthalpy ( $\Delta H_m^\circ$ ) considering a difference between specific heats in the glassy and rubbery states.

The equilibrium melting temperature ( $T_m^\circ$ ) was evaluated from the Gibbs–Thomson ( $T_m$  vs  $l_c^{-1}$ , where  $l_c$  is the lamella thickness obtained from SAXS) and Hoffman–Weeks plots ( $T_m$  vs  $T_c$ ). The equilibrium melting entropy ( $\Delta S_m^\circ$ ) was obtained from the relationship  $T_m^\circ = \Delta H_m^\circ/\Delta S_m^\circ$ . As a result, a smaller  $\Delta S_m^\circ$  of P(L-2H3MB) than PLLA was found to give a higher  $T_m$  of P(L-2H3MB).

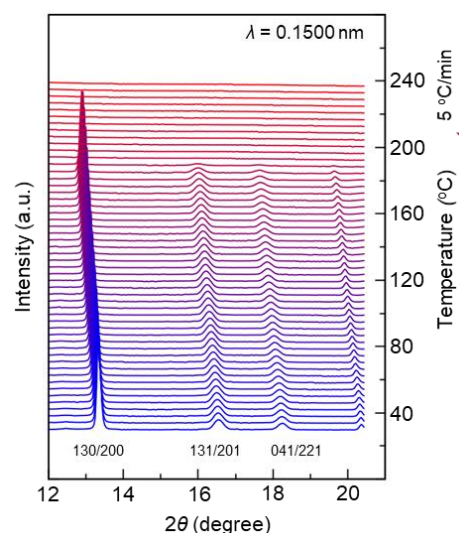


Fig. 1: TR-WAXD profiles during cooling process from the melt for P(L-2H3MB).

## Acknowledgement

This work was financially supported by the “Planting Seeds for Research” program from Tokyo Tech (2014–2015), Mizuho Foundation for the Promotion of Sciences (2015–2017), JSPS KAKENHI Grant-in-Aid for Young Scientists (B) 17K12836 (2017–2019), and Kanamori Foundation Research Grant (2018–2019).

## References

- [1] H. Marubayashi and S. Nojima, *Macromolecules* **49**, 5538 (2016).
- [2] H. Marubayashi, S. Nojima, *et al.*, *Polym. Degrad. Stabil.* **153**, 318 (2018).

\* hironori.marubayashi.d7@tohoku.ac.jp