Thermally stable polylactide stereocomplex conjugated by bio-based compound at both initiating and terminal groups

Hiroharu Ajiro,[1,2] Tran Hang Thi,[3] Tomoko Fujiwara,[4] Mitsuru Akashi[1,2]

[1]The Center for Advanced Medical Engineering and Informatics, Osaka University, Japan [2]Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Japan, [3]Faculty of Chemical Technology, Viet Tri University of Industry, Ministry of Industry and Trade, Tien Kien, Lam Thao, Phu Tho, Vietnam, [4]Department of Chemistry, The University of Memphis, TN 38152, USA

Introduction: Bio-based polymers has been studied for a long time, in order to improve their physical properties. Poly(lactide) (PLA) is one of the most intensively studied bio-based biodegradable polymers. Recently, 3,4-diacetoxycinnamic acid (DACA) has been introduced onto hydroxyl chain end of poly(L-lactide) (PLLA) to produce a highly thermal-stable polymer (DACA-PLLA)[1]. The DACA-PLLA improved T_{10}, which was the 10% weight loss temperature, over 100 ºC compared to that of PLLA with a same molecular weight. Actually, the DACA conjugation approach was also effective to improve T_{10} on other polymers, such as poly(ethylene glycol) and poly(ε-caprolactone).[2] It is important that the small chemical group, DACA, has improved the T_{10} values dramatically without affecting on the polymer main chain properties. However, the melting point (T_m~160 ºC) of DACA-PLLAs did not increase at all compared to the original PLLAs, and sometimes decreased.

In this study, we selected an approach of the stereocomplex formation using DACA-PLLA and DACA-PDLA, which were thermally stable against degradation. The mechanism of thermal stabilization of PLAs was discussed from the aspects of two factors: the degradation temperature (T_{10}) related to the chemical structure and the melting temperature (T_m) related to the crystal structure.

Methods: L-lactide (LLA; Musashino Chemical Laboratory, Ltd., Japan) and D-lactide (DLA; Musashino Chemical Laboratory, Ltd., Japan) were recrystallized from ethyl acetate, and then dried *in vacuo* at room temperature for 24h. Benzyl alcohol (Tokyo Chemical Industry, Ltd., Japan) was distilled with CaH_2 for purification. Thionyl chloride ($SOCl_2$), 3,4-dihydroxycinnamic acid (DHCA), acetic anhydride (Ac_2O) were used without purification.

The number average of molecular weight of PLLA was determined by size exclusion chromatography (SEC). A JASCO Chem NAV system was used with polystyrene standards at 40 ºC, equipped with PU-2080, AS-2055, CO-2065, and RI-2031. Two commercial columns (TSKgel SuperH4000 and TSKgel GMH_{XL}) were connected in series and tetrahydrofran (THF) was used as an eluent. ^{1}H NMR spectra were measured with a NMR spectrometer (JEOL FX400) at 400 MHz and 600MHz.

Results:

We have employed benzyl alcohol as an initiator to synthesize PLLA and PDLA, in order to incorporate an aromatic ring at one terminal, expecting π–π stacking interaction. Benzyl alcohol was selected because it is a natural product, one of the components of flower fragrances, such as roses. The polymer terminating part, a hydroxyl group at the chain end, was conjugated with DACA using reported procedure.[1] It is noteworthy that all of components, benzyl alcohol, lactides, and DACA, were derived from natural products. The number-average molecular weight (M_n) of PLLA and PDLA synthesized in this study were 8500 and 8300, which are abbreviated as DACA-PLLAb and DACA-PDLAb, implying benzyl group of the initiator (b). The initiating group was confirmed by ^{1}H NMR spectroscopy and FT-IR/ATR spectra. Figure 1 shows the conjugation of DACA to PLLAb. The vinyl groups were confirmed as an evidence of the introduction.

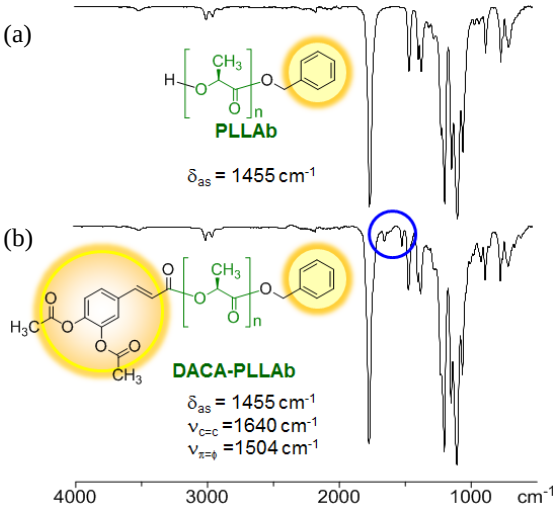

Figure 1. FT-IR/ATR spectra of PLLAb (a), DACA-PLLAb (b).

The thermal analyses of the DACA-PLLAb and DACA-PDLAb were analyzed by DSC and TGA. Mostly, DACA conjugation improved T_{10}values from about 230 ºC to 340 ºC, while almost no T_m temperature improvement. On the other hand, stereocomplex formation of DACA-PLLAb and DACA-PDLAb improved both T_m and T_{10} values. This tendency was also affected by the molecular weight of PLLA and PDLA.

Conclusions: The simultaneous improvement of the melting temperature (T_m=224ºC) and the decomposing temperature (T_{10}=359ºC) of poly(lactide)s was achieved by the stereocomplex formation of poly(L-lactide) and poly(D-lactide) with bio-based aromatic groups at both initiating and terminating chain ends.

References:

(1) T. H. Thi, M. Matsusaki and M. Akashi, *Chem. Commun.*, 2008, 3918–3920.

(2) T. H. Thi, M. Matsusaki, H. Hirano, H. Kawano, Y. Agari and M. Akashi, *J. Polym. Sci. Part A: Polym. Chem.*, 2011, **49**, 3152–3162.