

SUPPORTING INFORMATION

Facile Synthesis and Comparative Study of Poly(L-lactide) with Linear-Comb and Star-Comb Architecture

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Synthesis of Macroinitiator PB-OH

To achieve the graft PLLA with the targeted molecular weight via “graft-from” strategy, the corresponding precursor linear and star-shaped backbone with controlled number of hydroxyl groups need to be prepared first (Scheme S1).

Linear Hydroxylated Polybutadiene (IPB-OH). Polybutadiene (PB) of defined molecular weight was synthesized by anionic polymerization of butadiene with BuLi in cyclohexane in a flask at 50 °C for 3 h, quenched by the addition of excess methanol, and dried under vacuum. As we previously reported¹.

The PB product was then epoxidized to furnish a functional polymer containing randomly distributed epoxy groups on the backbone chain. The epoxidation reaction of PB was reported by Zuchowska² and changed some of the steps for design request. The mixture of Toluene (150 mL), formic acid (2.2 g) and PB (7.21 g) were placed in a 250 mL round-bottomed flask equipped with a dropping funnel and a magnetic stirring bar. H₂O₂ (6.63 g) solution in water (30 wt%) was added dropwise to the flask. The reaction was allowed to proceed for 2 h at 45 °C. The result solution was washed with deionized water until reached neutral (pH = 7). Then the polymer solution was concentrated by using a rotary evaporator and dried under vacuum at 40 °C to constant weight. The degree of epoxidation determined by the ¹H NMR was 18.64%³. PB was first epoxidized and then hydroxylated as follows: Predetermined quantities of epoxidized PB (IPBE, epoxidation degree was 18.64%, 11 g) and THF (1.14 mol, 82.08 g) were placed in a round-bottom flask equipped with a dropping funnel and magnetic stirrer. Solution of TfOH (2.8 mL) and water (10.26 g) was added dropwise into the reaction mixture at room temperature under mechanical agitation. After 3h, the reaction was terminated by pouring CHCl₃ (150 mL) into the flask and washed with deionized water for several times until the aqueous layer reached neutral (pH = 7). Then the polymer solution was concentrated by using a rotary evaporator and

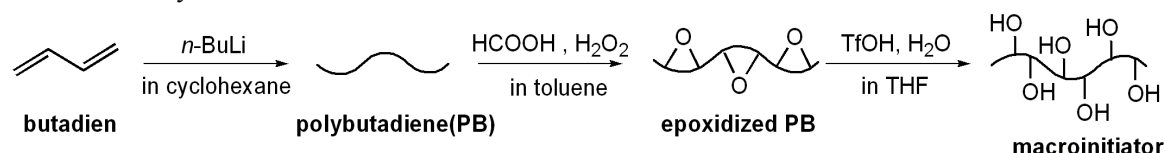
dried under vacuum at 40 °C to constant weight. The degree of hydroxylation determined by the ^1H NMR was 14.73%³.

The ^1H NMR spectrums involved in the preparation of IPB-OH main chain are depicted in Figure S1.

Four-arm Star-shaped Hydroxylated Polybutadiene (sPB-OH). The procedure for preparing the star brush involved the addition of SiCl_4 as a coupling agent at the end of the polymerization of PB to obtain the four-armed PB. As follows: Living PBLi was synthesized as indicated above, without quenched. The coupling agent SiCl_4 was added into the mixture via a syringe. After another 3 h, the reaction was quenched with degassed 2-propanol. Then remove the solvent and dried the crude polymer under vacuum at 40 °C over night to constant weight.

The rest of the process was the same as that described for the linear PB-OH initiator.

Scheme S1. Synthesis of linear PB-OH macroinitiator.



^1H NMR spectrum of an epoxidized PB was showed in Figure S1(2). The two new peaks at 2.9 and 2.7 ppm indicated the presence of *cis*- and *trans*-1,4 epoxy protons respectively⁴. As olefinic hydrogens were being converted into epoxidic ones, the calculations were made by the following equation:

Pre-determination of the epoxidation degree of PB using methyltrioxorhenium- $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}_2$ biphasic catalytic system:

$$E = \frac{A(2.7) + A(2.9)}{A(2.7) + A(2.9) + A(4.9) + A(5.4) - 0.5A(4.9)} \times 100\% \quad (1)$$

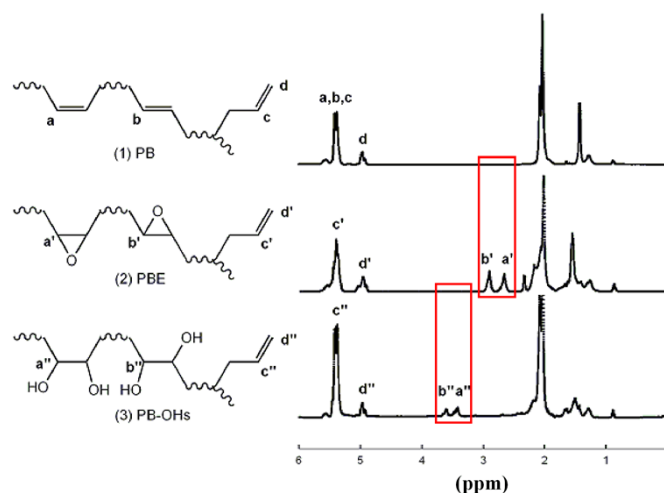


Figure S1. ^1H NMR spectra of macroinitiator PB-OHs: (1) PB (2) Epoxidized PB (PBE,

18.64 %) (3) Hydroxylated PB (PB-OHs, 14.73 %).

Scheme S2. Synthesis of linear-comb PLLA (lcPLLA) macromolecule by ROP.

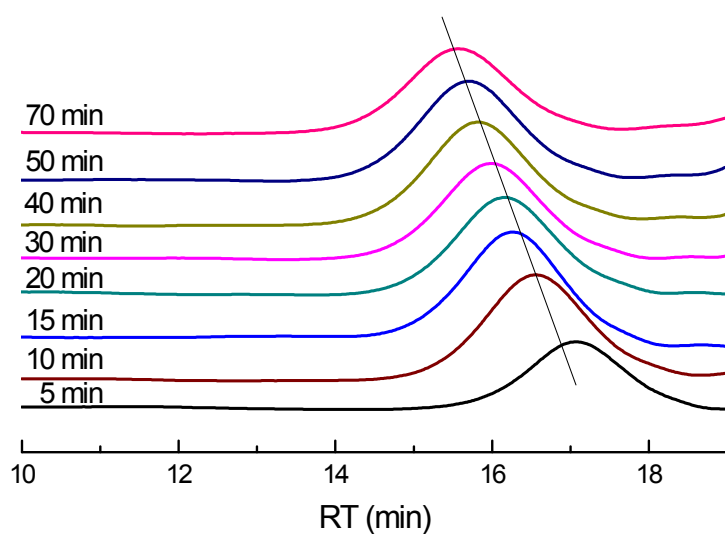
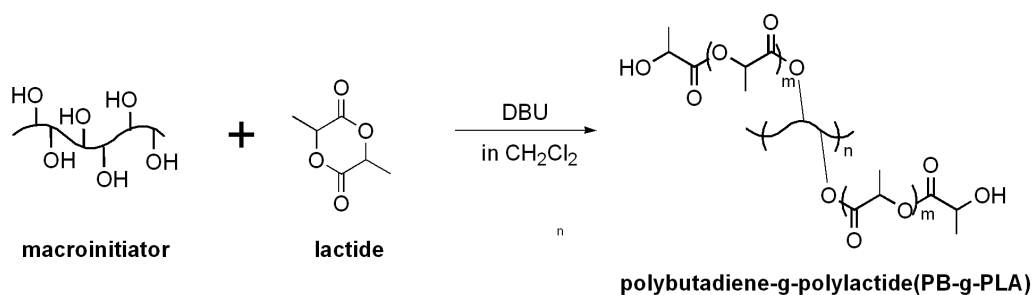


Figure S2. GPC spectrum of graft PLLA at different reaction time.

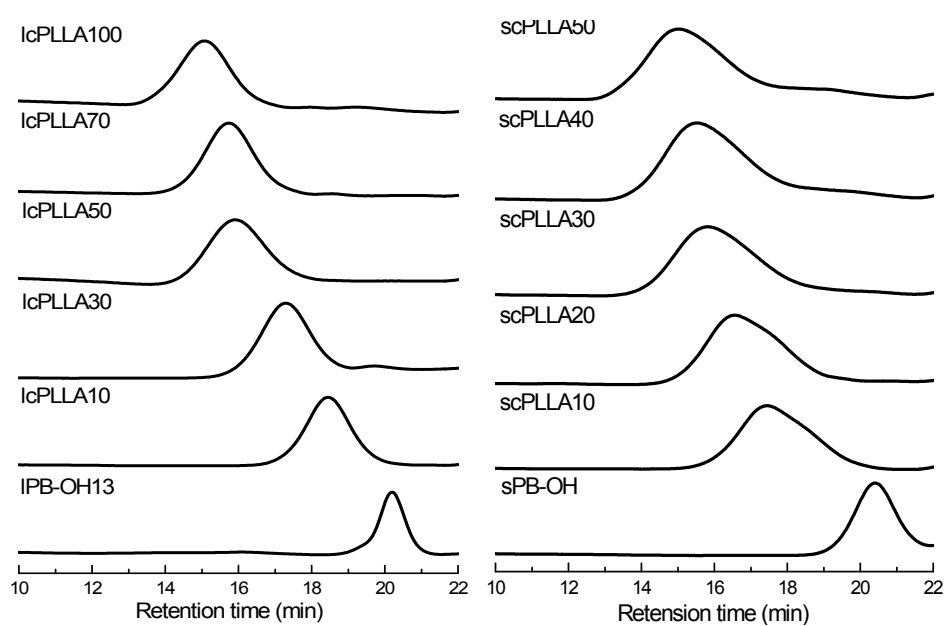


Figure S3. GPC spectrum of linear-comb and star-comb graft PLLA.

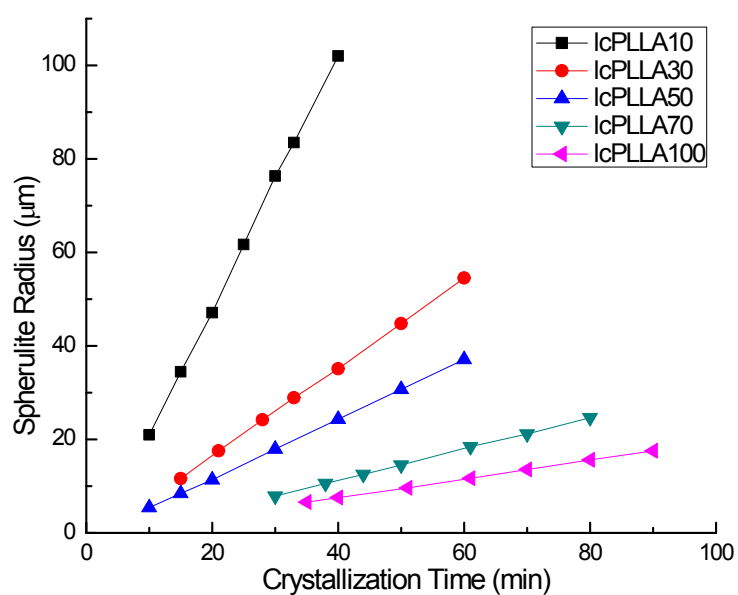


Figure S4. Spherulite growth radius increased linearly with time at 110 °C.

References

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