Supporting Information

Chemo-enzymatic synthesis of Poly(lactate-*co*-(3-hydroxybutyrate)) by a LA-polymerizing enzyme

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Fig. S1 Confirmation of ester exchange between TP in LATP and CoA by using HPLC.





Before

After 72 h

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Fig. S2 Photographs of the reaction mixture before and after reaction, left: before reaction; right: after
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72 h. White precipitate was formed after 72 h.



Fig. S3 TLC analysis of the organic solvent phase before and after reaction, (a): before reaction; (b) after 72 h. Thiophenol released with the progress of reaction was observed in the organic solvent phase after the reaction.



Fig. S4 ¹H-NMR spectra of the products obtained from the reaction mixture containing (R)-LATP or (S)-LATP and (R)-3HBTP as substrate precursors. (a): (R)-LATP and (R)-3HBTP; (b): (S)-LATP and (R)-3HBTP.



Fig. S5 GPC chart of P(LA-*co*-3HB) obtained from the reaction mixture containing (*R*)-LATP and (*R*)-3HBTP as substrate precursors and $C_{Ps}(STQK)$ as a catalyst, respectively.



Fig. S6 ¹H-NMR spectra of the product obtained from the reaction mixture containing the same amounts of (*R*)-LATP and (*R*)-3HBTP as substrate precursors. (a): normal figure (0 -7.0 ppm) ; (b): enlarged figure (4.8 - 5.5 ppm).



Fig. S7 ¹H-NMR spectra of the product obtained from the reaction mixture containing the same amounts of (*R*)-LATP and (*R*)-3HBTP as substrate precursors. (a): enlarged figure (2.3 -2.9 ppm) ; (b): enlarged figure (1.1 - 1.7 ppm).