Supporting Information

Synthesis of a New Poly([R]-3-hydroxybutyrate) RAFT Agent

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Figure S1. ¹H NMR of purified natural PHB in CDCl₃



Figure S3. Integral values of specific peaks in ¹H NMR of macro PHB-CTA in CDCl₃



Figure S4. ¹H NMR of macro mono-hydroxylated PHB-CTA in CDCl₃



Figure S5. ¹H NMR of PHB-*b*-PDMAEMA copolymer synthesized by RAFT method in CDCl₃

Transesterification reaction

Overall reaction: 1 nat. PHB + 300 hex-OH \rightarrow x PHB-OH (mono-hydroxylated PHB) (S1)

The rate of reaction (r) can be expressed as:

$$r = -r_{nat. PHB} = \frac{-r_{hex}}{300} = \frac{r_{PHB-OH}}{x}$$
 (S2)

$$r = -\frac{dC_{nat.PHB}}{dt} = -\left(\frac{1}{300}\right)\frac{dC_{hex}}{dt} = \left(\frac{1}{x}\right)\frac{dC_{PHB-OH}}{dt}$$
(S3)

Where r = reaction rate, $-r_{nat,PHB}$ = rate of disappearance of natural PHB, $-r_{hex}$ = rate of disappearance of 1hexanol, r_{PHB-OH} = rate of appearance of PHB-OH, $C_{nat, PHB}$ = the concentration of natural PHB, C_{hex} = the concentration of 1-hexanol, C_{PHB-OH} = the concentration of PHB-OH, respectively. The reaction rate (r) can be written in terms of rate constant (k) as:

$$r = kC_{nat.PHB}^{m}C_{hex}^{n}$$
(S4)

$$\frac{dC_{nat.PHB}}{dt} = k_p \frac{d[Es]}{dt}$$
(S5)

Where k_p is a proportionality constant, and *Es* refers to the fractional/remaining ester bonds (%) at time *t* given by Eq. (S6):

$$E_{S} = \frac{\text{Number of ester bond at time t}}{\text{Initial number of ester bond}} \times 100\%$$
(S6)

Number of ester bond can be derived by Eq. (S7):

If we defined that

Number of ester bond =
$$\frac{Mn \text{ of polymer chain} - Mw \text{ of transesterification agent}}{Molar mass of 1 repeating HB unit}$$
 (S7)

Firstly, if the reaction is zero order, it is assumed that the rate of reaction (k) is independent of the concentration of the reactants. The reaction rate (r) was given in terms of the rate constant (k), and the disappearing of ester bonds in natural purified PHB over a period of time is given as follow, when m = n = 0, combine equation (S3), (S4) and (S5):

$$r = k = -\frac{d[Es]}{dt}k_p \tag{S8}$$

k and k_p are constants and can be summed together become new *k*. Integration of equation (8) gives: $[Es]_t = -kt + [Es]_0$ (S9)

Where $[Es]_t$ represents the number of ester bonds at time *t*, and $[Es]_{\theta}$ represents the initial number of ester bonds in the natural purified PHB. A plot of $[Es]_t$ vs. time gives a straight line with a slope of (-k), if the reaction follow a zero order reaction. However, based on the plots in Figure S6, the reaction is not following zero order.

(a) mono-hydroxylated PHB at 120 °C (b) mono-hydroxylated PHB at 130 °C (c) mono-hydroxylated PHB at 140 °C



Figure S6. Zero order plot ([Es] vs. time)

Secondly, if the reaction is first order, it means that the reaction rate (r) is proportional to the concentration of one reactant. For a first order reaction, its reaction rate (r) is given as follow, when m=1 and n=0 combine equation (S3), (S4) and (S5):

$$r = -\frac{d[Es]}{dt}k_p = k [Es]$$
(S10)

k and k_p are constants and can be summed together become new k. Integration of first order rate law: $ln_{100}^{100}[Es]_t = -kt + ln_{100}^{100}[Es]_0$ (S11)

A plot of $\ln[\text{Es}]_t$ vs. time gives a straight line with a slope of (-k), if the reaction follow a first order reaction. Based on the plots in Figure S7, the reaction is also not following first order.



e S7. First order plot (ln [Es]_t vs. time) with linear fit with initial point at y-axis fixed at $\ln(100) = 4.605$. Lastly, if the reaction is assumed to be second order reaction, it means that the reaction rate (r) is proportional to the concentration of one second order reactant, or two first order reactants. It is assumed that r depends on the concentration of one second order reactant (*i.e.* ester bonds in PHB). The relationship of r and k are given as follow, when m=2, n=0, combine equation (S3), (S4) and (S5):

$$r = -\frac{d[Es]}{dt}k_p = -k [Es]^2$$
(S12)

k and k_p are constants and can be summed together become new k. Integration of second order rate law:

$$\frac{1}{[Es]_t} = \frac{1}{[Es]_0} + kt$$
(S13)

A plot of $1/[Es]_t$ vs. time gives a straight line with a slope of k, if the reaction follow a second order reaction. The plot was shown in Figure S8.



Figure S8. Kinetic study of transesterification reaction – second order model fitting (1/[Es] *vs.* time plot at (a) 120 °C, (b) 130 °C, (c) 140 °C)