Supporting Information:

Degradable Poly(ethylene oxide) Through Metal-Free Copolymerization of Ethylene Oxide with L-Lactide

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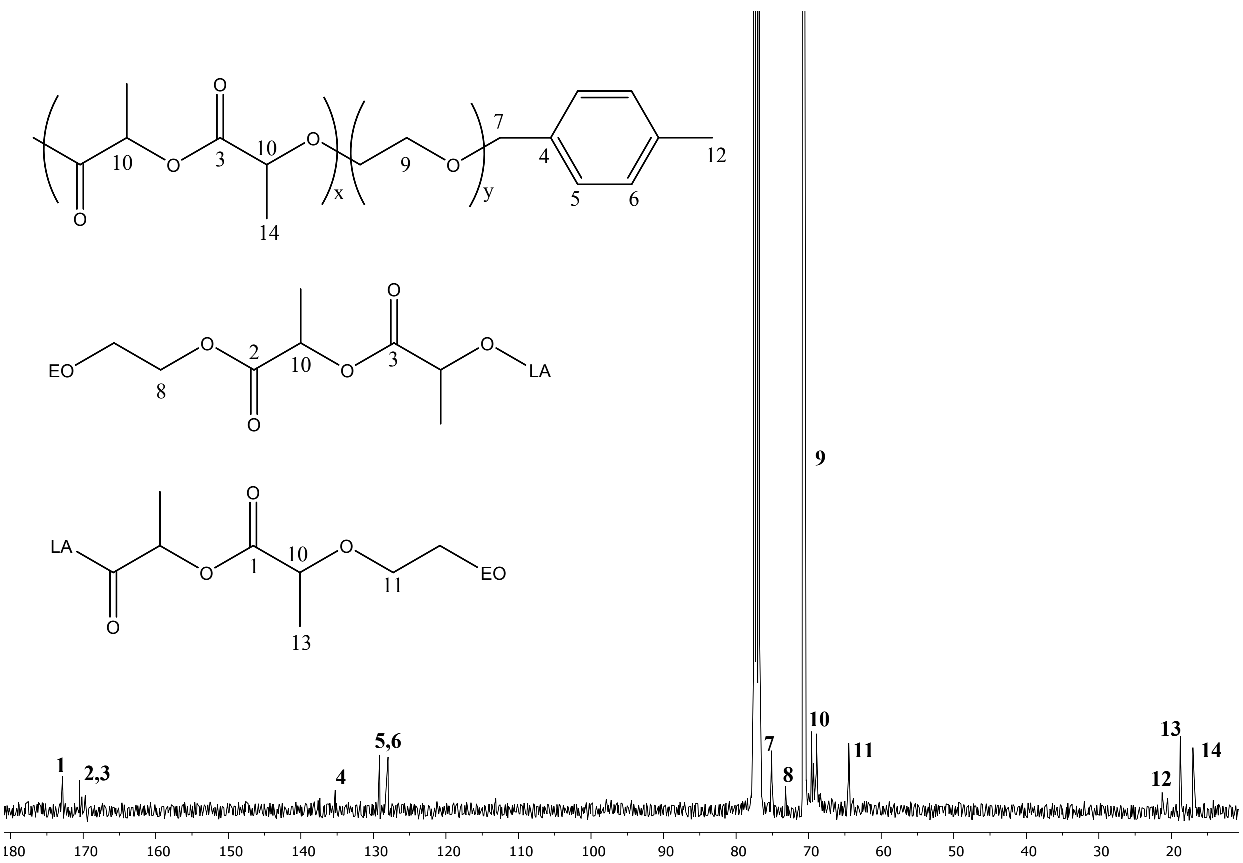

Figure S1: ^{13}C NMR spectrum of P(EO-*co*-LLA) random copolymer (entry 9 of Table 1).

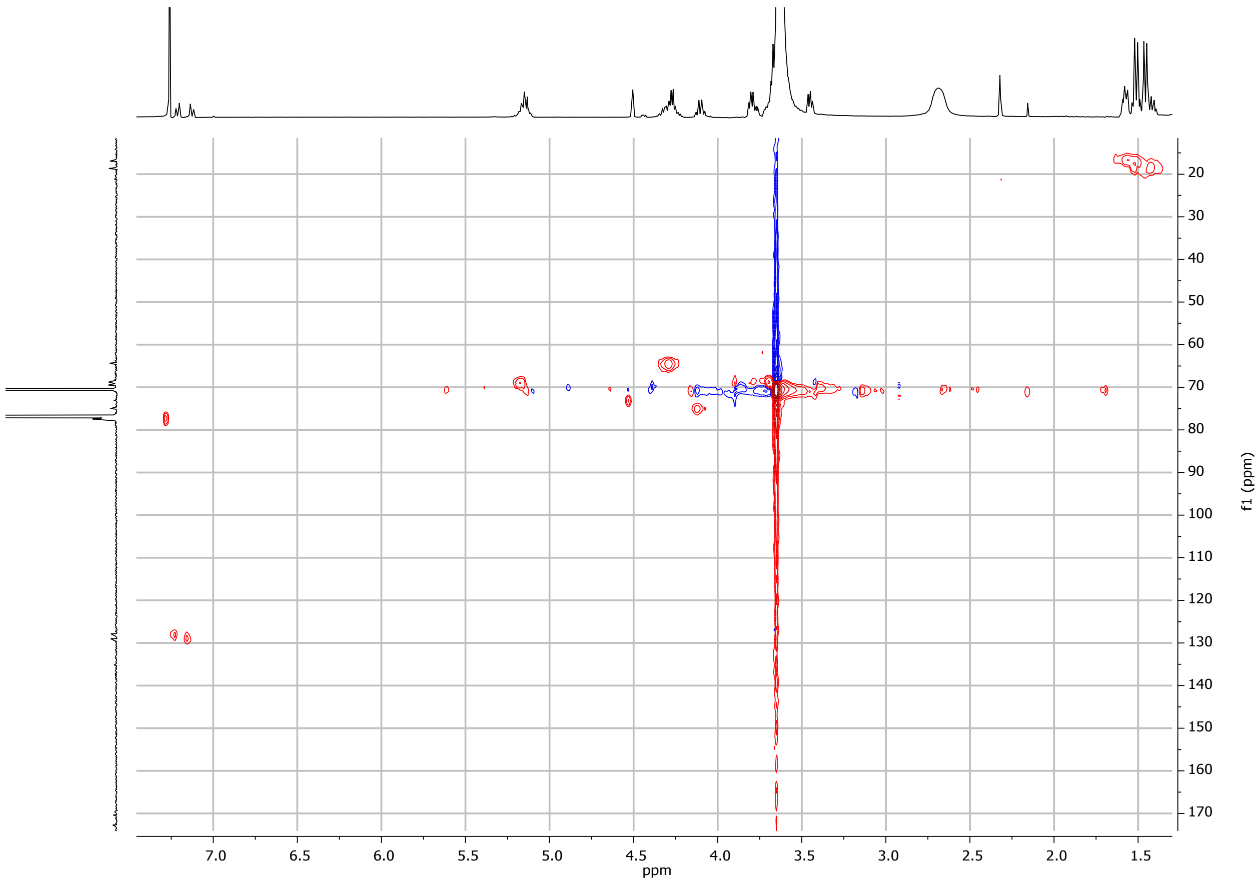

Figure S2: HSQC spectrum of P(EO-*co*-LLA) random copolymer (entry 9 of Table 1).

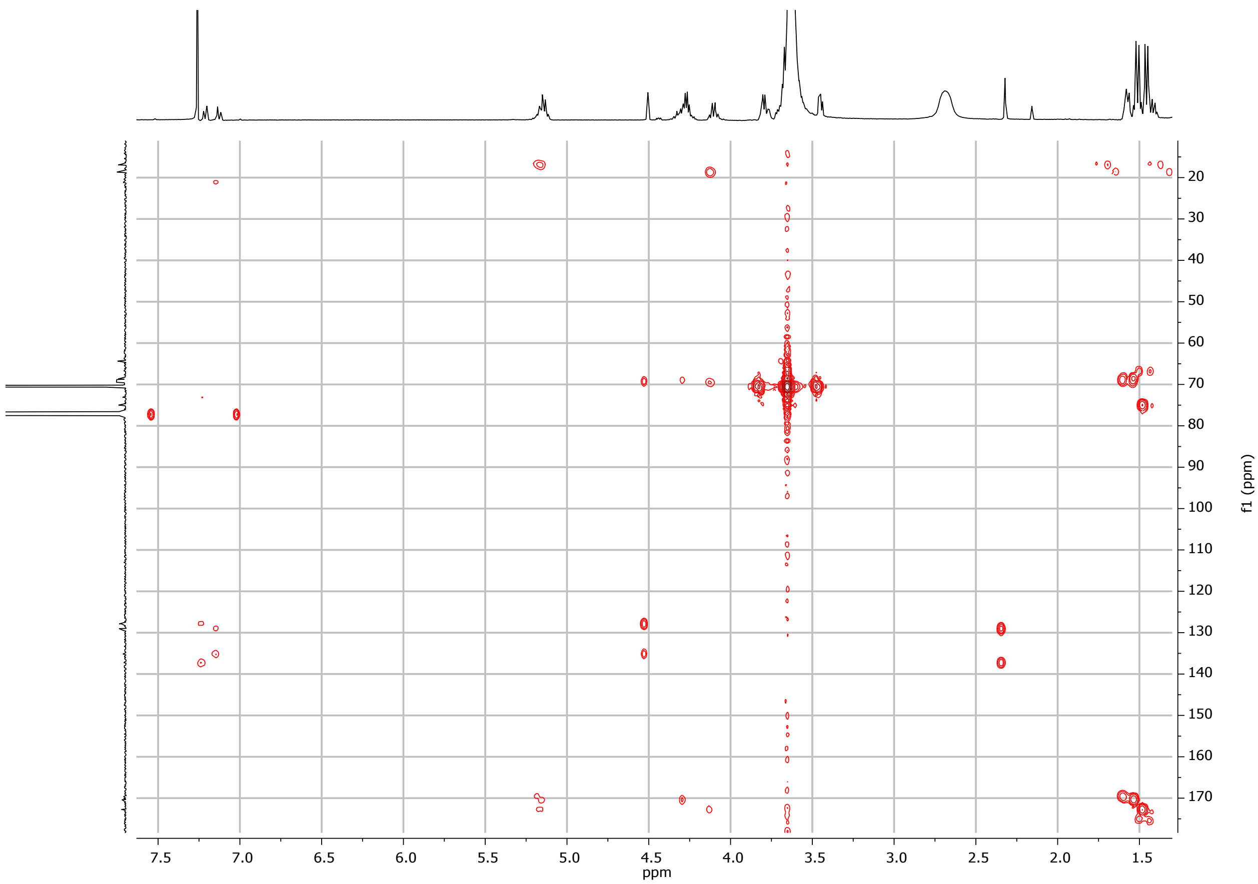

Figure S3: HMBC spectrum of P(EO-*co*-LLA) random copolymer (entry 9 of Table 1).

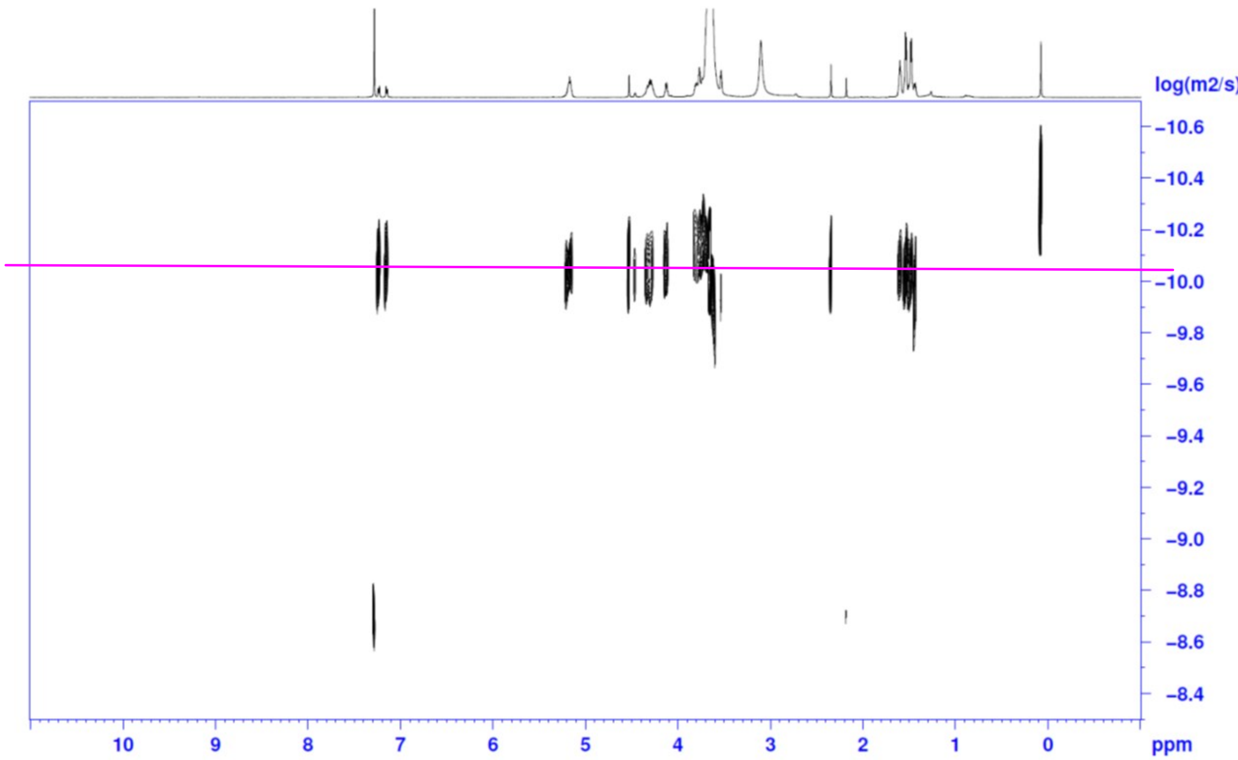

Figure S4: DOSY spectrum of P(EO-*co*-LLA) random copolymer (entry 9 of Table 1).

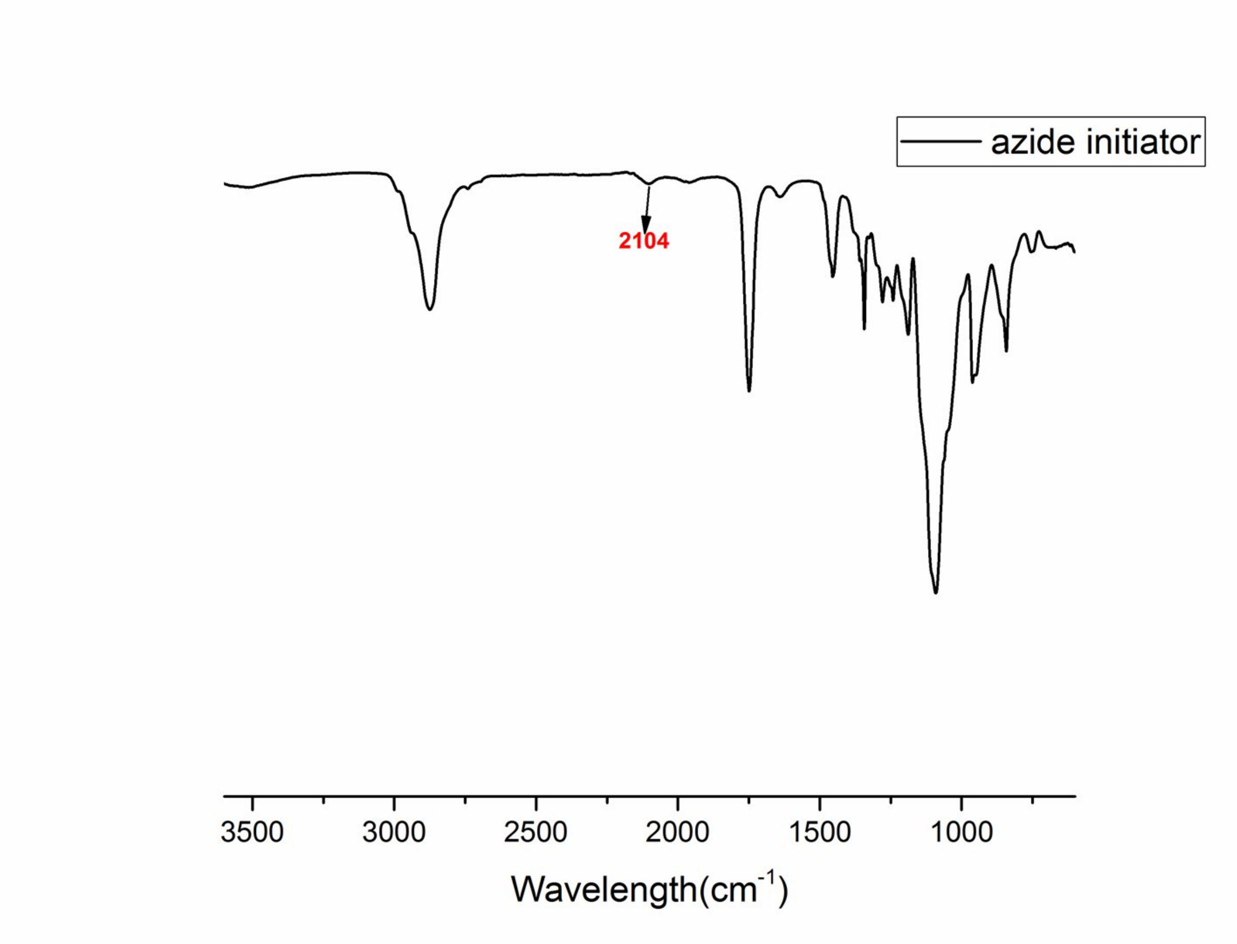

Figure S5: IR Data of showing azide incorporation on copolymer (entry 21, Table 1).

Reactivity Ratio Calculation by Non terminal Model of BSL [1]

$$r_a = \frac{ln[\frac{[1 - P_{ab} - (1 - n_a)(1 - P_b)]}{n_a}]}{ln(1 - P_b)} \quad ……………………………………….(1)$$

$$r_b = \frac{ln[\frac{[(1 - P_{ab} - n_a(1 - P_a)]}{1 - n_a}]}{ln(1 - P_a)} \quad …………………………………………..(2)$$

For PMBA/ P_4 system

(Entry 1, Table 2)

$[EO]_0$ = 6.1 n_a = 0.87 EO conversion P_a = 0.28 LLA conversion P_b = 0.055

$[LLA]_0$ = 0.9 n_b = 0.13 P_{ab} = 0.25 Ester cont ent (^{1}HNMR) = 2.50%

On applying this values in equations (1) & (2)

r_a = 5.78 r_b = 0.15

(Entry 2, Table 2)

$[EO]_0$ = 6.1 n_a = 0.87 EO conversion P_a = 0.44 LLA conversion P_b = 0.091

$[LLA]_0$ = 0.9 n_b = 0.13 P_{ab} = 0.39 Ester content (^{1}HNMR) = 3.12%

On applying this values in equations (1) & (2)

r_a = 5.97 r_b = 0.1

(Entry 3, Table 2)

$[EO]_0$ = 6.1 n_a = 0.87 EO conversion P_a = 0.65 LLA conversion P_b = 0.18

$[LLA]_0$ = 0.9 n_b = 0.13 P_{ab} = 0.59 Ester content (^{1}HNMR) = 4.12%

On applying this values in equations (1) & (2)

$r_a = 5.30$ $r_b = 0.2$

(Entry 4, Table 2)

$[EO]_0 = 6.1$ $n_a = 0.87$ EO conversion $P_a = 0.775$ LLA conversion $P_b = 0.27$

$[LLA]_0 = 0.9$ $n_b = 0.13$ $P_{ab} = 0.71$ Ester content (^{1}HNMR) = 4.98%

On applying this values in equations (1) & (2)

$r_a = 4.75$ $r_b = 0.22$

(Entry 5, Table 2)

$[EO]_0 = 6.1$ $n_a = 0.87$ EO conversion $P_a = 0.99$ LLA conversion $P_b = 0.52$

$[LLA]_0 = 0.9$ $n_b = 0.13$ $P_{ab} = 0.93$ Ester content (^{1}HNMR) = 6.09%

On applying this values in equations (1) & (2)

$r_a = 5.07$ $r_b = 0.19$

On taking average

$r_a = 5.37 \pm 0.40$ $r_b = 0.17 \pm 0.04$

For TBACl System

(Entry 6, Table 2)

$EO]_0 = 3.4$ $n_a = 0.83$ EO conversion $P_a = 0.44$ LLA conversion $P_b = 0.21$

$[LLA]_0 = 0.69$ $n_b = 0.17$ $P_{ab} = 0.4$ Ester content (^{1}HNMR) = 9.15%

On applying this values in equations (1) & (2)

$r_a = 2.45$ $r_b = 0.4$

(Entry 7, Table 2)

$EO]_0 = 3.4$ $n_a = 0.83$ EO conversion $P_a = 0.58$ LLA conversion $P_b = 0.32$

$[LLA]_0 = 0.69$ $n_b = 0.17$ $P_{ab} = 0.54$ Ester content (^{1}HNMR) = 10.1%

On applying this values in equations (1) & (2)

r_a = 2.28 r_b = 0.42

(Entry 8, Table 2)

EO]$_0$ = 3.4 n_a = 0.83 EO conversion P_a = 0.72 LLA conversion P_b = 0.45

[LLA]$_0$ = 0.69 n_b = 0.17 P_{ab} = 0.67 Ester content (^{1}HNMR) = 11.5%

On applying this values in equations (1) & (2)

r_a = 2.1 r_b = 0.44

(Entry 9, Table 2)

EO]$_0$ = 3.4 n_a = 0.83 EO conversion P_a = 0.8 LLA conversion P_b = 0.57

[LLA]$_0$ = 0.69 n_b = 0.17 P_{ab} = 0.76 Ester content (^{1}HNMR) = 13.1%

On applying this values in equations (1) & (2)

r_a = 1.9 r_b = 0.52

(Entry 10, Table 2)

EO]$_0$ = 3.4 n_a = 0.83 EO conversion P_a = 0.89 LLA conversion P_b = 0.75

[LLA]$_0$ = 0.69 n_b = 0.17 P_{ab} = 0.87 Ester content (^{1}HNMR) = 14.5%

On applying this values in equations (1) & (2)

r_a = 1.62 r_b = 0.67

On taking average

r_a = 2.07± 0.25 r_b = 0.49±0.08

For PPNCl System

(Entry 11, Table 2)

EO]$_0$ = 3.4 n_a = 0.83 EO conversion P_a = 0.56 LLA conversion P_b = 0.1

[LLA]$_0$ = 0.69 n_b = 0.17 P_{ab} = 0.48 Ester content (^{1}HNMR) = 3.52%

On applying this values in equations (1) & (2)

r_a = 7.75 r_b = 0.11

(Entry 12, Table 2)

EO]$_0$ = 3.4 n_a = 0.83 EO conversion P_a = 0.73 LLA conversion P_b = 0.17

[LLA]$_0$ = 0.69 n_b = 0.17 P_{ab} = 0.64 Ester content (^{1}HNMR) = 4.50%

On applying this values in equations (1) & (2)

r_a = 7.15 r_b = 0.17

(Entry 13, Table 2)

EO]$_0$ = 3.4 n_a = 0.83 EO conversion P_a = 0.855 LLA conversion P_b = 0.267

[LLA]$_0$ = 0.69 n_b = 0.17 P_{ab} = 0.75 Ester content (^{1}HNMR) = 6.03%

On applying this values in equations (1) & (2)

r_a =6.08 r_b = 0.14

(Entry 14, Table 2)

EO]$_0$ = 3.4 n_a = 0.83 EO conversion P_a = 0.937 LLA conversion P_b = 0.34

[LLA]$_0$ = 0.69 n_b = 0.17 P_{ab} = 0.83 Ester content (^{1}HNMR) = 7.12%

On applying this values in equations (1) & (2)

r_a = 6.29 r_b = 0.13

(Entry 15, Table 2)

EO]$_0$ = 3.4 n_a = 0.83 EO conversion P_a = 0.96 LLA conversion P_b = 0.41

[LLA]$_0$ = 0.69 n_b = 0.17 P_{ab} = 0.86 Ester content (^{1}HNMR) = 8.05%

On applying this values in equations (1) & (2)

r_a = 5.78 r_b = 0.14

On taking average

$r_a = 6.61 \pm 0.67$ $r_b = 0.14 \pm 0.01$

Reactivity Ratio Calculation by Terminal Model of Meyer Lowry [2]

$$conv. = 1 - \left(\frac{f_1}{f_1^{\,0}}\right)^{r_2/(1-r_2)}\left(\frac{1-f_1}{1-f_1^0}\right)^{r_1/(1-r_1)} \times \left(\frac{f_1(2-r_1-r_2)-r_2-1}{f_1^0(2-r_1-r_2)-r_2-1}\right)^{(r_1r_2-1)/(1-r_1)(1-r_2)}$$

Assuming copolymer is of pure gradient character, $r_1r_2 = 1$, the last term in above equation equals to 1.

$$conv. = 1 - \left(\frac{f_1}{f_1^{\,0}}\right)^{r_2/(1-r_2)}\left(\frac{1-f_1}{1-f_1^0}\right)^{r_1/(1-r_1)}$$

$$1 - conv. = \left(\frac{f_1}{f_1^{\,0}}\right)^{r_2/(1-r_2)}\left(\frac{1-f_1}{1-f_1^0}\right)^{r_1/(1-r_1)}$$

Take logarithm for both sides,

$$log(1 - conv.) = \frac{r_2}{1-r_2}\log\left(\frac{f_1}{f_1^{\,0}}\right) + \frac{r_1}{1-r_1}log(\frac{1-f_1}{1-f_1^0})$$

Replace r_1 by $1/r_2$,

$$\log(1-conv.) = \frac{r_2}{1-r_2}\log\left(\frac{f_1}{f_1^{\,0}}\right) + \frac{1}{r_2-1}log(\frac{1-f_1}{1-f_1^0})$$

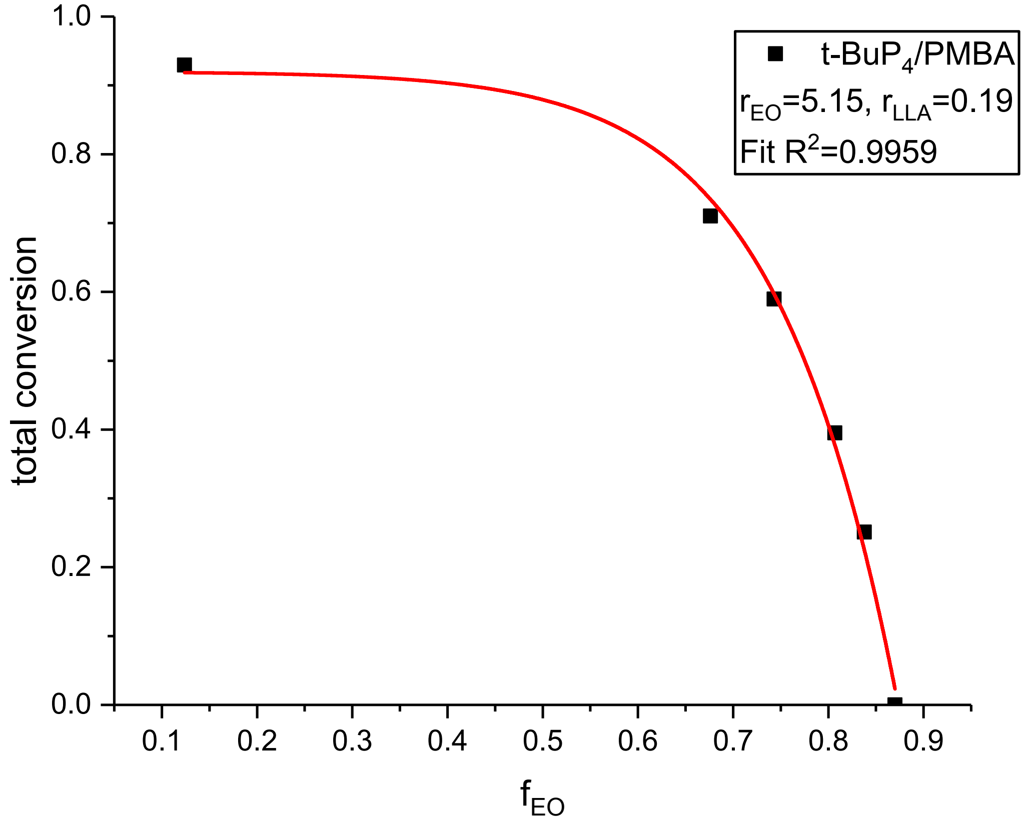

Figure S6: Terminal model of ML for the determination of reactivity ratios of copolymerization of EO and LLA initiated with t-BuP$_4$/PMBA in the presence of triethylborane (Entry 1,2,3,4,5 of Table 2).

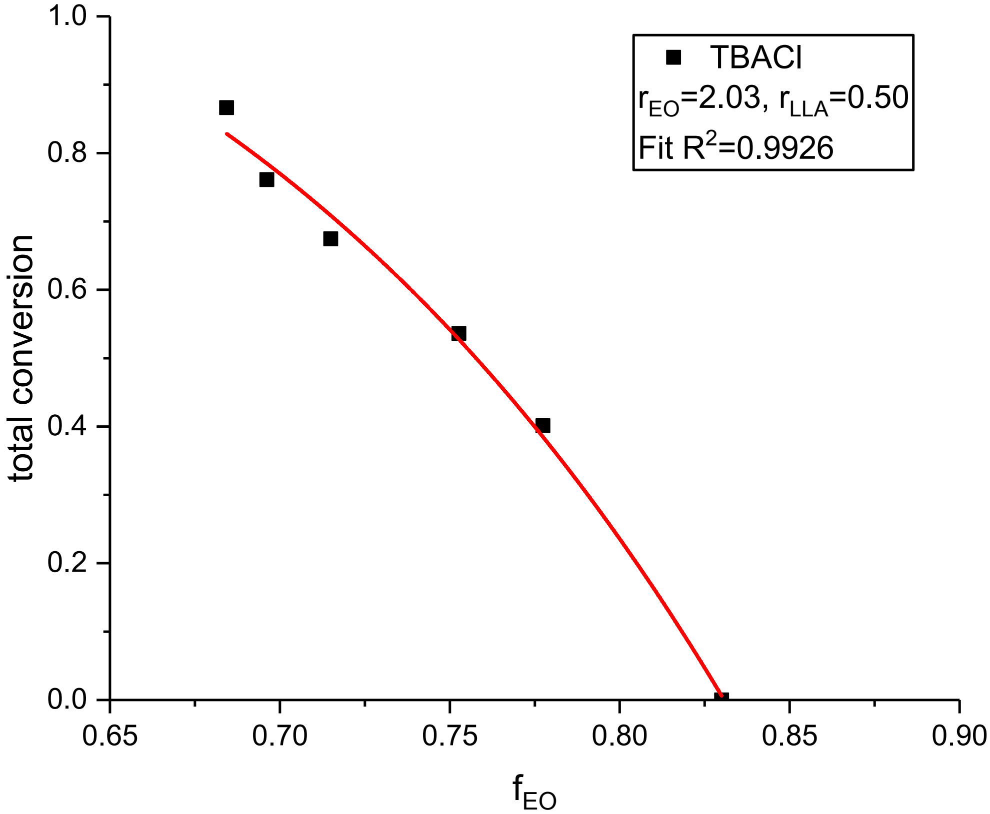

Figure S7: Terminal model of ML for the determination of reactivity ratios of copolymerization of EO and LLA initiated with TBACl in the presence of triethylborane (Entry 6,7,8,9,10 of Table 2).

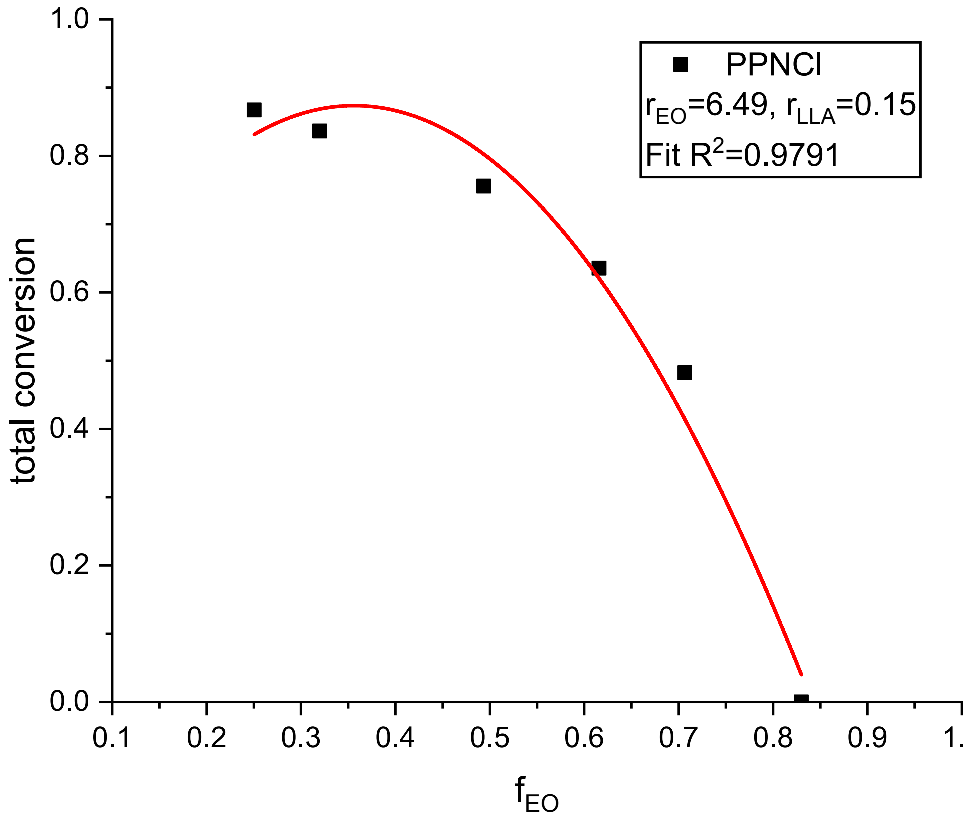

Figure S8: Terminal model of ML for the determination of reactivity ratios of copolymerization of EO and LLA initiated with PPNCl in the presence of triethylborane (Entry 11,12,13,14,15 of Table 2).

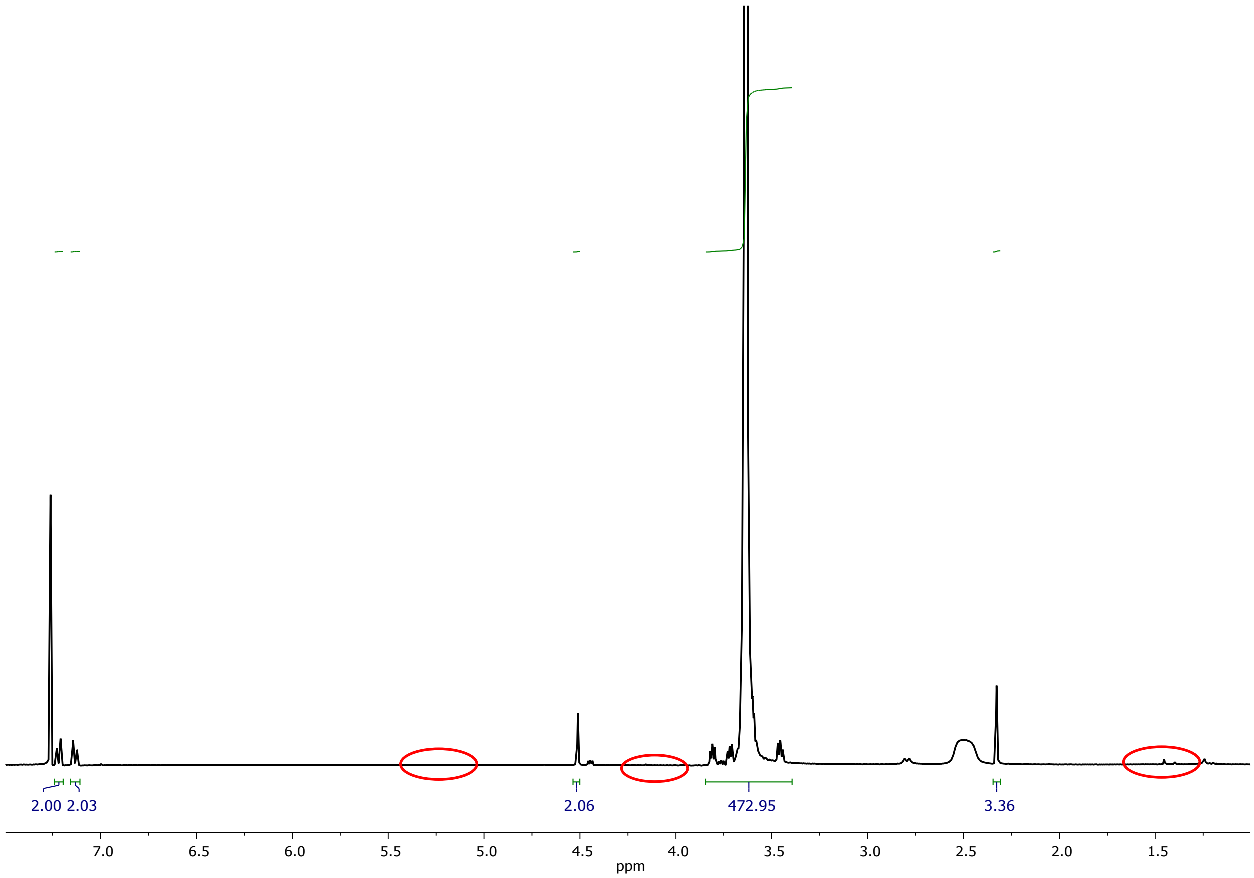

Figure S9: Represent ^{1}H NMR spectrum of P(EO-*co*-LLA) random copolymer after degradation (entry 12 of Table 1).

1. B. S. Beckingham, G. E. Sanoja and N. A. Lynd, *Macromolecules*, 2015, **48**, 6922-6930.
2. (a) N. A. Lynd, R. C. Ferrier and B. S. Beckingham, *Macromolecules*, 2019, **52**, 2277-2285; (b) V. E. Meyer and G. G. Lowry, *J. Polym. Sci. Part A: Gen. Pap.*, 1965, **3**, 2843-2851; (c) F. T. Wall, *J. Am. Chem. Soc.*, 1944, **66**, 2050-2057.