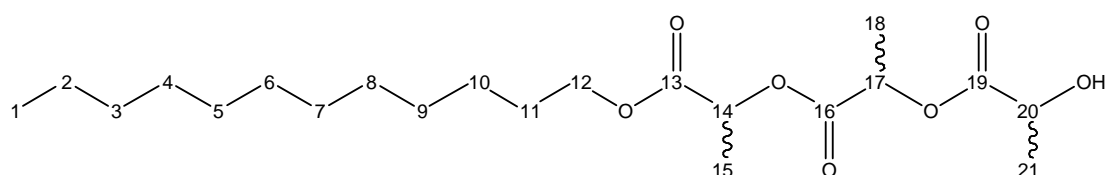


Appendix 1: ^{13}C NMR assignments of Poly(lactic acid) Polymers Initiated by long chain alcohols.

A. Polymers Catalysed by Stannous Octanoate.

1.A1.: Dodecanol Initiated Polymerisation of Lactide



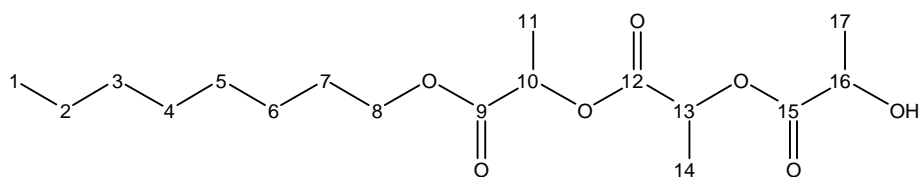
Gh17-03 (Dodecanol : L-lactide; 1 : 3): ^{13}C NMR (CDCl_3 , 75 Mhz) (important characteristic peaks) δ (ppm): 66.10 & 66.24(CH_2O , C-12), 67.10($\text{CH}(\text{CH}_3)\text{OH}$, C-20), 69.41 & 69.71($\text{CH}(\text{CH}_3)\text{O}$, C-14,17), 169.93($\text{C}=\text{O}$, C-16,19), 170 & 170.55($\text{C}=\text{O}$, C-13) and 175.55(COOH).

Gh17-06 (Dodecanol : L-lactide; 1 : 2): ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) δ (ppm): 65.71 & 65.84(CH_2O , C-12), 66.71($\text{CH}(\text{CH}_3)\text{OH}$, C-20), 69.04, 69.32 & 69.44($\text{CH}(\text{CH}_3)\text{O}$, C-14,17), 169.53 & 169.60($\text{C}=\text{O}$, C-16,19), 170.16($\text{C}=\text{O}$, C-13) and 175.15(COOH).

Gh17-24a (Dodecanol : L-lactide; 1 : 50): ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) δ (ppm):

Gh17-24b (Dodecanol : L-lactide; 1 : 50): ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) δ (ppm): 69.40, 69.58 & 69.81($\text{CH}(\text{CH}_3)\text{O}$, C-14,17), 72.86(unreacted lactide), 167.79($\text{C}=\text{O}$, C-13), 169.77($\text{C}=\text{O}$, C-16), 170.02($\text{C}=\text{O}$, C-19)

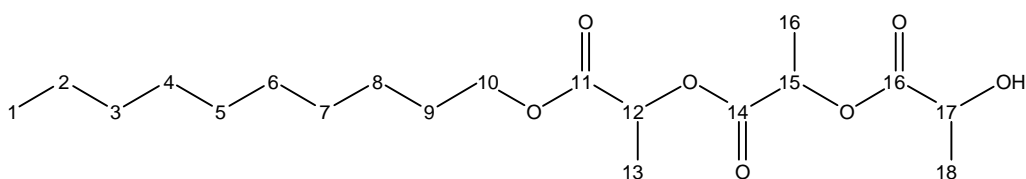
1.A2: Octanol Initiated Polymerisation of Lactide



Gh17-08 (Octanol : L-lactide; 1 : 3): ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 14.06(CH_3 , C-1), 16.63, 16.73 & 16.82(CH_3 , C-11,14), 20.49(CH_3 , C-17), 22.60(CH_2 , C-2), 25.72(CH_2 , C-6), 28.45(CH_2 , C-7), 29.12(CH_2 , C-4,5), 31.73(CH_2 , C-3), 65.70 & 65.83(CH_2O , C-8), 66.71($\text{CH}(\text{CH}_3)\text{OH}$, C-16), 69.02, 69.32 & 69.43($\text{CH}(\text{CH}_3)\text{O}$, C-10,13), 169.53, 169.6 & 169.68($\text{C}=\text{O}$, C-12,15), 170.13($\text{C}=\text{O}$, C-9) and 175.13(COOH)

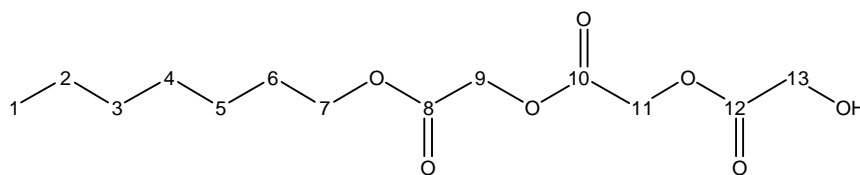
Gh17-13 (Octanol : L-lactide; 1 : 2): ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) δ (ppm): 63.44(CH_2OH , unreacted alcohol), 66.13 & 66.22(CH_2O , C-8), 67.12($\text{CH}(\text{CH}_3)\text{OH}$, C-16), 69.80($\text{CH}(\text{CH}_3)\text{O}$, C-10,13) and 176.26(COOH)

1.A3: Decanol Initiated Polymerisation of Lactide



Gh17-33b (Decanol : rac-lactide; 1 : 3): ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) δ (ppm): 14.49(CH_3 , C-1), 16.16(lactide), 17.05, 17.12 & 17.19(CH_3 , C-13,16), 20.42 & 20.87(CH_3 , C-18), 23.05(CH_2 , C-2), 26.11(CH_2 , C-8), 28.83 & 28.91(CH_2 , C-4,7,9), 29.54, 29.66 & 29.86(CH_2 , C-5,6), 32.25(CH_2 , C-3), 66.09 & 66.21(CH_2O , C-10), 67.10($\text{CH}(\text{CH}_3)\text{OH}$, C-17), 69.41, 69.58, 69.71 & 69.81($\text{CH}(\text{CH}_3)\text{O}$, C-12,15), 169.55 & 169.75($\text{C}=\text{O}$, C-14,16), 170.01 & 170.57($\text{C}=\text{O}$, C-11).

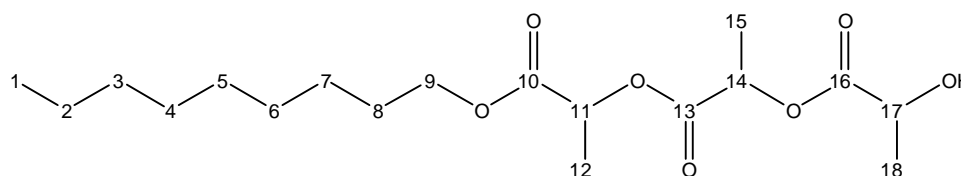
1.A4: Heptanol Initiated Polymerisation of Glycolide



Gh17-76 (Heptanol : glycolide; 1 : 6): ^{13}C NMR (d_6 -Acetone, 75 MHz) (important characteristic peaks) δ (ppm): 61.09, 61.22 & 61.38(CH_2OH , C-13), 61.74, 61.84, 62.00, 62.20 & 62.28(CH_2O , C-9,11), 65.49, 66.13 & 66.30(CH_2O , C-7), 167.91($\text{C}=\text{O}$), 168.38($\text{C}=\text{O}$) and 173.25($\text{C}=\text{O}$).

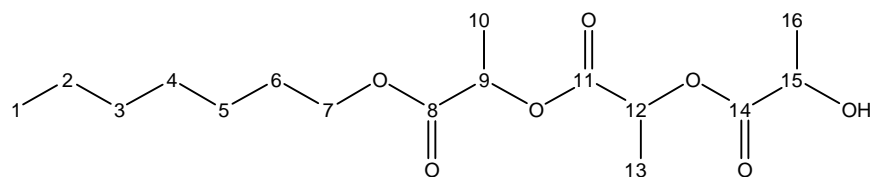
Gh17-76 (Heptanol : glycolide; 1 : 6): ^{13}C NMR (d_3 -Acetonitrile, 75 MHz) (important characteristic peaks) δ (ppm): 59.40 & 59.65(CH_2OH , C-13), 60.22, 60.75 & 61.23(CH_2O , C-9,11), 65.11 & 65.25(CH_2O , C-7), 166.78($\text{C}=\text{O}$), 167.24($\text{C}=\text{O}$) and 172.06($\text{C}=\text{O}$).

1.A6: Nonanol Initiated Polymerisation of Lactide



Gh17-77 (Nonanol : rac-lactide; 1 : 6): ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 14.10(CH_3 , C-1), 15.81(CH_3), 16.67 & 16.74(CH_3 , C-12,15), 20.52(CH_3 , C-18), 22.85(CH_2 , C-2), 25.73(CH_2 , C-7), 28.45(CH_2 , C-8), 29.17(CH_2 , C-4,6), 29.43(CH_2 , C-5), 31.83(CH_2 , C-3), 65.70(CH_2O , C-9), 66.66 & 66.71($\text{CH}(\text{CH}_3)\text{OH}$, C-17), 69.02, 69.19 & 69.32($\text{CH}(\text{CH}_3)\text{O}$, C-11,14), 169.17, 169.38 and 169.63($\text{C}=\text{O}$).

1.A5: Heptanol initiated polymerisation of lactide

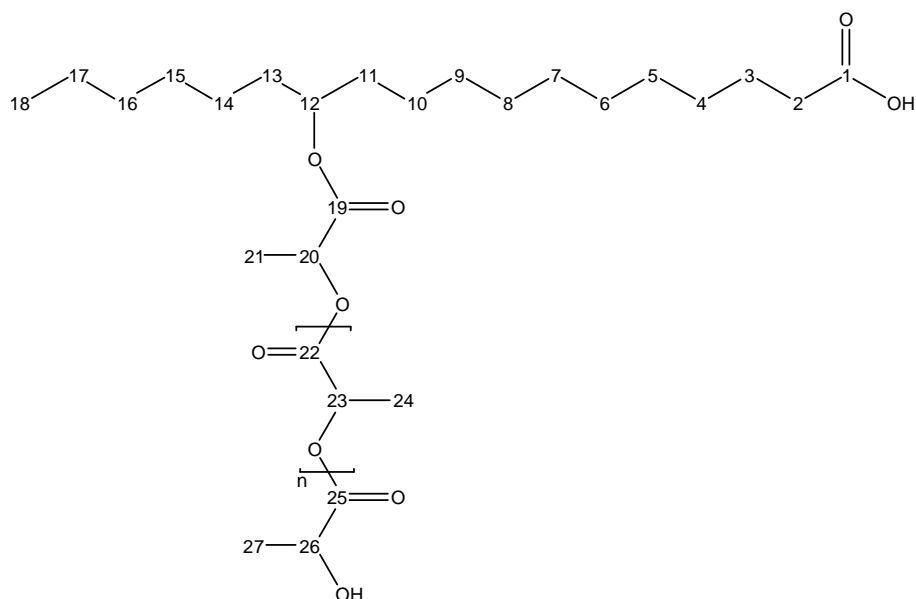


Gh17-82a (5 mins) (Heptanol : rac-lactide; 1 : 3): ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) $\delta(\text{ppm})$: 66.08(CH_2O , C-7), 67.04 & 67.09($\text{CH}(\text{CH}_3)\text{OH}$, C-15), 69.43, 69.59, 69.72 & 69.81($\text{CH}(\text{CH}_3)\text{O}$, C-9,12), 72.85(lactide), 169.56, 169.76 & 170.02($\text{C}=\text{O}$), 170.59($\text{C}=\text{O}$) and 175.53(COOH).

Gh17-82c (20 mins) (Heptanol : rac-lactide; 1 : 3): ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) $\delta(\text{ppm})$: 66.08 & 66.21(CH_2O , C-7), 67.04 & 67.09($\text{CH}(\text{CH}_3)\text{OH}$, C-15), 69.43, 69.58, 69.71 & 69.81($\text{CH}(\text{CH}_3)\text{O}$, C-9,12), 169.56, 169.76 & 170.02($\text{C}=\text{O}$), 170.59($\text{C}=\text{O}$) and 175.53(COOH)

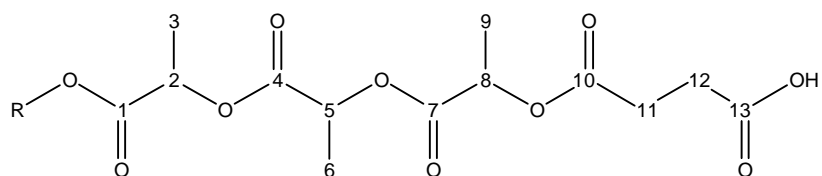
Gh17-82f (80 mins) (Heptanol : rac-lactide; 1 : 3): ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) $\delta(\text{ppm})$: 66.08 & 66.21(CH_2O , C-7), 67.03 & 67.09($\text{CH}(\text{CH}_3)\text{OH}$, C-15), 69.43, 69.58, 69.71 & 69.80($\text{CH}(\text{CH}_3)\text{O}$, C-9,12), 169.56, 169.76 & 170.02 ($\text{C}=\text{O}$), 170.59($\text{C}=\text{O}$) and 175.53(COOH).

1.A6: 12-Hydroxystearic Acid Initiated Polymerisation of Lactide.



Gh17-79 (12-HSA : rac-lactide; 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) $\delta(\text{ppm})$: 67.05, 67.10 ($\text{CH}(\text{CH}_3)\text{OH}$, C-26), 69.40, 69.59 & 69.82($\text{CH}(\text{CH}_3)\text{O}$, C-20,23), 76.42(CH-O , C-12), 169.58, 169.75, 170.03 and (C=O).

1.A7: Polymers End Capped by Ring Opening Metathesis of Succinic Anhydride.



Gh17-86 (heptanol : rac-lactide : succinic anhydride; 1 : 20 : 1) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) $\delta(\text{ppm})$:

Gh17-87b (20 mins) (heptanol : rac-lactide : succinic anhydride; 1 : 3 : 1) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) $\delta(\text{ppm})$: 65.69(CH_2O , C-R), 66.65 & 66.63($\text{CH}(\text{CH}_3)\text{OH}$, C-8), 68.63($\text{CH}(\text{CH}_3)\text{O}$, C-8), 69.02, 69.19, 69.33 & 69.43($\text{CH}(\text{CH}_3)\text{O}$, C-2,5), 169.37 & 169.56(C=O), 170.20(C=O), 170.87(C=O), 171.63(C=O , C-10) and 175.14(COOH).

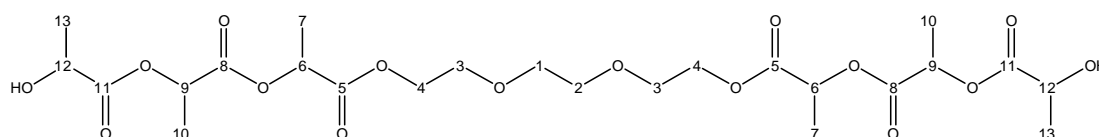
Gh17-87d (30 mins) (heptanol : rac-lactide : succinic anhydride; 1 : 3 : 1) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) $\delta(\text{ppm})$: 65.70(CH_2O , C-R), 66.71($\text{CH}(\text{CH}_3)\text{OH}$, C-8), 68.65($\text{CH}(\text{CH}_3)\text{O}$, C-8), 69.01, 69.20 & 69.33($\text{CH}(\text{CH}_3)\text{O}$, C-2,5), 169.37, 169.63, 169.98 & 170.21($\text{C}=\text{O}$), 171.61($\text{C}=\text{O}$, C-10) and 177.13(COOH , C-13).

Gh17-87f (80 mins) (heptanol : rac-lactide : succinic anhydride; 1 : 3 : 1) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) $\delta(\text{ppm})$: 65.70(CH_2O , C-R), 66.66($\text{CH}(\text{CH}_3)\text{OH}$, C-8), 68.65($\text{CH}(\text{CH}_3)\text{O}$, C-8), 69.01, 69.20 & 69.33($\text{CH}(\text{CH}_3)\text{O}$, C-2,5), 169.38, 169.66, 169.98 & 170.22($\text{C}=\text{O}$), 171.61($\text{C}=\text{O}$, C-10) and 177.32(COOH , C-13).

Gh17-88 (heptanol : rac-lactide : succinic anhydride; 1 : 6 : 1) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) $\delta(\text{ppm})$: 65.70(CH_2O , C-R), 68.66($\text{CH}(\text{CH}_3)\text{O}$, C-8), 69.01, 69.19 & 69.33($\text{CH}(\text{CH}_3)\text{O}$, C-2,5), 169.17, 169.38 & 169.63($\text{C}=\text{O}$).

Gh17-89 (12-HSA : rac-lactide : succinic anhydride; 1 : 6 : 1) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) $\delta(\text{ppm})$: 68.61($\text{CH}(\text{CH}_3)\text{O}$, C-8), 69.01, 69.20 and 69.44($\text{CH}(\text{CH}_3)\text{O}$, C-2,5), 169.19, 169.36, 169.63 and 169.99($\text{C}=\text{O}$).

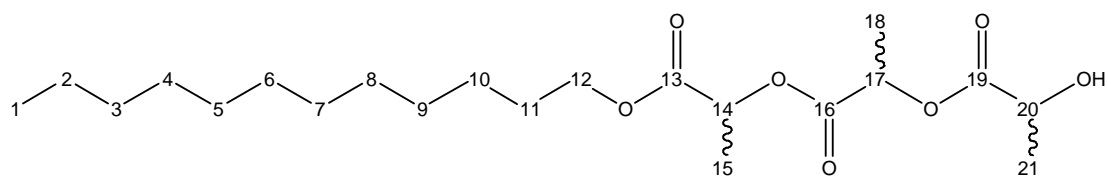
1.A8: PEG₁₀₀₀-PLA copolymers.



Gh17-92 (PEG₁₀₀₀ : rac-lactide; 1 : 50) ^{13}C NMR (CDCl_3 , 75 MHz) $\delta(\text{ppm})$: 15.82(CH_3 , C-7,10), 16.67(CH_3 , C-7,10), 20.52(CH_3 , C-13), 64.43(CH_2O , C-4), 69.00 & 69.19($\text{CH}(\text{CH}_3)\text{O}$, C-6,9), 70.55(CH_2O , C-1,2), 169.16, 169.37 and 169.63 ($\text{C}=\text{O}$).

B: Polymers Initiated by DMAP and long chain alcohols in Solution.

1.B1: Dodecanol Initiated Polymers of *rac*-Lactide.



Gh17-14 (Dodecanol : *rac*-lactide; 1 : 3) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) ppm: 66.09(CH_2O , C-12), 67.07($\text{CH}(\text{CH}_3)\text{OH}$, C-20), 69.41, 69.17 & 69.77($\text{CH}(\text{CH}_3)\text{O}$, C-14,17), 169.93, 170.00, 170.11 & 170.55($\text{C}=\text{O}$) and 175.51(COOH). DMAP peaks at 39.83, 106.82 and 145.44.

Gh17-16 (Dodecanol : *rac*-lactide; 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) ppm: 66.10(CH_2O , C-12), 67.09($\text{CH}(\text{CH}_3)\text{OH}$, C-20), 69.42, 69.58 & 69.71($\text{CH}(\text{CH}_3)\text{O}$, C-14,17), 169.77 & 170.02($\text{C}=\text{O}$). DMAP peaks at 39.84, 106.85 and 145.74.

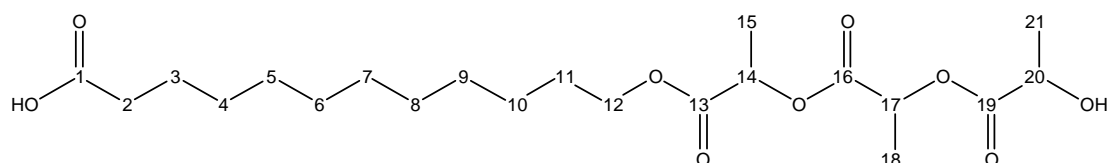
Gh17-17 (Dodecanol : *rac*-lactide; 1 : 10) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) ppm: 66.10(CH_2O , C-12), 67.10($\text{CH}(\text{CH}_3)\text{OH}$, C-20), 69.41, 69.17 & 69.87($\text{CH}(\text{CH}_3)\text{O}$, C-14,17), 72.87(unreacted lactide) 169.77 & 170.02($\text{C}=\text{O}$). DMAP peaks at 39.76, 106.91 and 146.76.

Gh17-18 (Dodecanol : *rac*-lactide; 1 : 20) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) ppm: 66.10(CH_2O , C-12), 67.10($\text{CH}(\text{CH}_3)\text{OH}$, C-20), 69.41, 69.58 & 69.71($\text{CH}(\text{CH}_3)\text{O}$, C-14,17), 169.55, 169.76 & 170.01 ($\text{C}=\text{O}$). DMAP peaks at 39.88 and 106.87.

Gh17-21 (Dodecanol : *rac*-lactide; 1 : 50) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) ppm: 69.40 & 69.58($\text{CH}(\text{CH}_3)\text{O}$, C-14,17), 169.55, 169.77 & 170.02($\text{C}=\text{O}$). DMAP peaks at 39.80, 106.88 and 146.19.

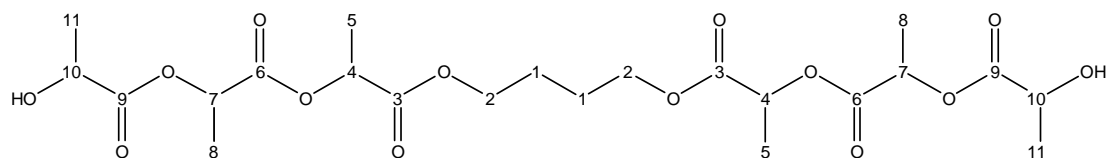
Gh17-23 (Dodecanol : *rac*-lactide; 1 : 100) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) ppm: 69.39 & 69.57($\text{CH}(\text{CH}_3)\text{O}$, C-14,17), 72.87(unreacted lactide), 167.87, 169.55, 169.76, 169.82 & 170.01($\text{C}=\text{O}$). DMAP peaks at 40.02, 106.90 and 144.25.

1.B2: 12-Hydroxydodecanoic Acid Initiated Polymerisation of *rac*-Lactide.



Gh17-15 (12-hydroxydodecanoic acid : *rac*-lactide; 1 : 3) ^{13}C NMR(CDCl_3 , 75 MHz) ppm: 16.18 (CH_3), 17.06, 17.13, 17.22 & 17.71(CH_3 , C-15,18), 20.88(CH_3 , C-21), 25.15(CH_2 , C-3), 26.10(CH_2 , C-10), 28.82(CH_2 , C-4,11), 29.45, 29.52, 29.61, 29.76 & 29.81(CH_2 , C-5-10), 34.42(CH_2 , C-2), 66.10(CH_2O , C-12), 67.11($\text{CH}(\text{CH}_3)\text{OH}$, C-20), 69.45, 69.60 & 69.73($\text{CH}(\text{CH}_3)\text{O}$, C-14,17), 72.87(unreacted lactide), 167.84, 169.78, 170.02 & 170.58($\text{C}=\text{O}$), 175.57(COOH) and 178.94(COOH).

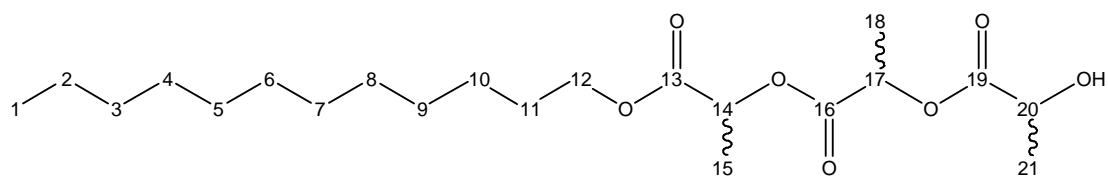
1.B3: 1,4-butanediol Initiated Polymerisation of *rac*-Lactide.



Gh17-27 (1,4-butanediol : *rac*-lactide; 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz) ppm: 17.01 17.10 & 17.15(CH_3 , C-5,8), 20.84 (CH_3 , C-11), 25.36(CH_2 , C-1), 65.16(CH_2O , C-2), 66.96 & 67.02($\text{CH}(\text{CH}_3)\text{OH}$, C-10), 69.37, 69.54 & 69.63($\text{CH}(\text{CH}_3)\text{O}$, C-4,7), 169.72, 169.79, 169.97, 170.13 & 170.43($\text{C}=\text{O}$) and 175.44(COOH).

C: Polymers Catalysed by DMAP in a Melt Polymerisation.

1.C1: Dodecanol initiated polymers.



Gh17-28 (Dodecanol : *rac*-lactide; 50 : 1) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) ppm: 67.00 & 67.06($\text{CH}(\text{CH}_3)\text{OH}$, C-20), 69.39, 69.57 & 69.86($\text{CH}(\text{CH}_3)\text{O}$, C-14, 17), 169.55, 169.75, 169.81 and 170.00 (C=O). DMAP peaks at (39.00, 106.89 and 145.17).

Gh17-31a (Dodecanol : *rac*-lactide; 1 : 3) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) ppm: 65.06 (CH_2O , C-12), 67.08($\text{CH}(\text{CH}_3)\text{OH}$, C-20), 68.36, 69.40 & 69.69($\text{CH}(\text{CH}_3)\text{O}$, C-14, 17), 168.66 (C=O). DMAP peak at (106.85)

Gh17-31b (Dodecanol : *rac*-lactide; 1 : 3) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) ppm: 66.10 & 66.21(CH_2O , C-12), 67.10($\text{CH}(\text{CH}_3)\text{OH}$, C-20), 69.41, 69.57, 69.70 & 69.81($\text{CH}(\text{CH}_3)\text{O}$, C-14, 17), 169.75, 170.01 and 170.57 (C=O). DMAP peaks at (39.79, 106.84 and 145.97).

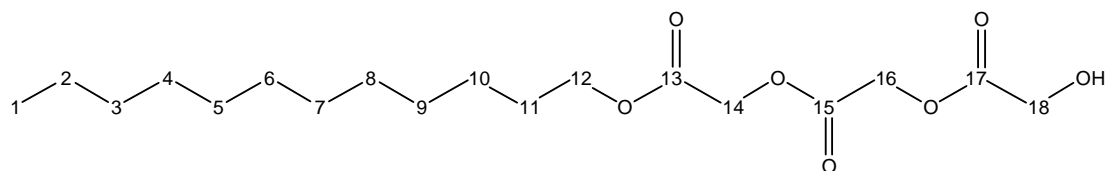
Gh17-31c (Dodecanol : *rac*-lactide; 1 : 3) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) ppm: 66.09 & 66.18(CH_2O , C-12), 67.10($\text{CH}(\text{CH}_3)\text{OH}$, C-20), 69.40, 69.56, 69.70 & 69.80($\text{CH}(\text{CH}_3)\text{O}$, C-14, 17), 169.76 and 170.57 (C=O). DMAP peaks at (39.85, 106.81 and 145.12).

Gh17-32a Dodecanol : *rac*-lactide; 1 : 20) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) ppm: 66.09(CH_2O , C-12), 67.08($\text{CH}(\text{CH}_3)\text{OH}$, C-20), 69.39, 69.57, 69.70 & 69.81($\text{CH}(\text{CH}_3)\text{O}$, C-14, 17), 169.76 and 170.01 (C=O). DMAP peaks at (39.74, 106.86 and 146.61).

Gh17-32b (Dodecanol : *rac*-lactide; 1 : 20) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) ppm: 66.09(CH_2O , C-12), 67.09($\text{CH}(\text{CH}_3)\text{OH}$, C-20), 69.39, 69.57, 69.70 & 69.81($\text{CH}(\text{CH}_3)\text{O}$, C-14, 17), 169.76 and 170.02 ($\text{C}=\text{O}$). DMAP peaks at (39.82, 106.84).

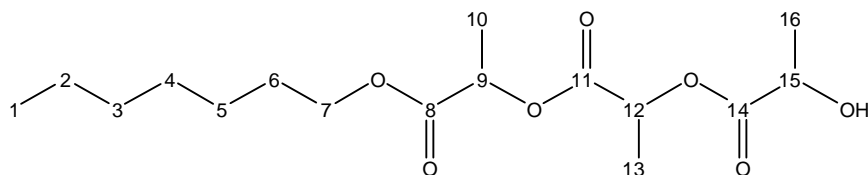
Gh17-45 (Dodecanol : *rac*-lactide : lauric acid; 1 : 3 : 1) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) ppm: 66.10 & 66.23(CH_2O , C-12), 67.10($\text{CH}(\text{CH}_3)\text{OH}$, C-20), 69.42, 69.57, 69.71 & 69.81($\text{CH}(\text{CH}_3)\text{O}$, C-14, 17), 169.76 ($\text{C}=\text{O}$) and 178.40 (COOH). DMAP peaks at (39.74, 106.86 and 146.61).

1.C2: Dodecanol Initiated Polymerisation of Glycolide.



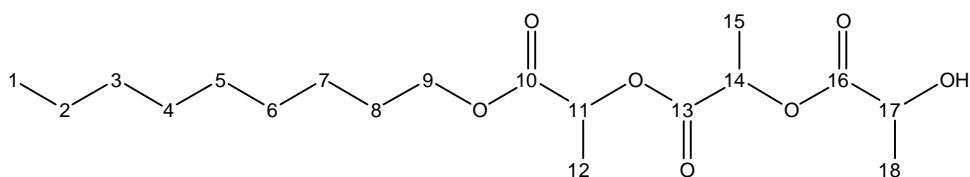
Gh17-50 (Dodecanol : glycolide; 1 : 3) ^{13}C NMR (CDCl_3 , 75 MHz) ppm: 14.52(CH_3 , C-1), 23.08(CH_2 , C-2), 26.14(CH_2 , C-10), 28.84 & 28.93(CH_2 , C-4,9,11), 29.57, 29.74, 29.87, 29.94 & 30.02(CH_2 , C-5,6,7,8) 32.30(CH_2 , C-3), 60.80 & 60.96(CH_2OH , C-18), 61.22, 61.55, 61.65 & 61.86(CH_2O , C-14,16), 64.20(CH_2O , glycolide), 66.15, 66.24 & 66.30(CH_2O , C-12). DMAP peaks at (40.18, 106.81 and 142.19).

1.C3: Heptanol Initiated Polymerisation of Lactide.



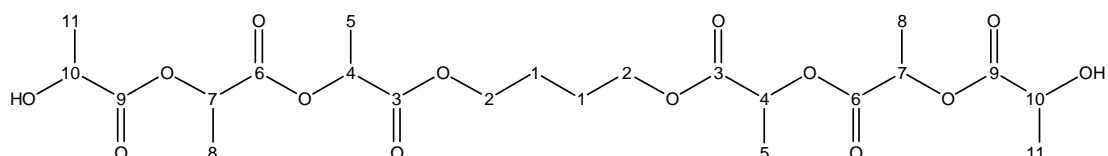
Gh17-37 (Heptanol : *rac*-lactide; 1 : 3) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) ppm: 66.09 & 66.21(CH_2O , C-7), 67.10($\text{CH}(\text{CH}_3)\text{OH}$, C-15), 69.42, 69.57, 69.71 & 69.82($\text{CH}(\text{CH}_3)\text{O}$, C-9, 12), 169.76 ($\text{C}=\text{O}$). DMAP peaks at (39.67, 106.88 and 147.31).

1.C4: Nonanol Initiated Polymerisation of Lactide.



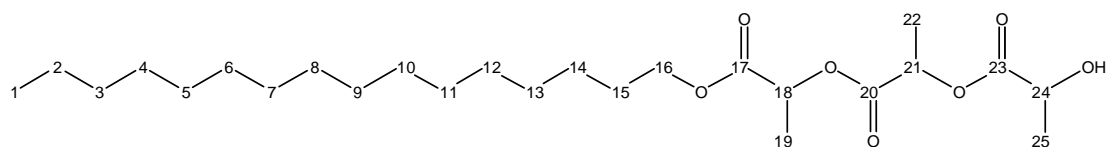
Gh17-35 (Nonanol : *rac*-lactide; 1 : 3) ^{13}C NMR (CDCl_3 , 75 MHz) (important characteristic peaks) ppm: 66.08 & 66.20(CH_2O , C-9), 67.08($\text{CH}(\text{CH}_3)\text{OH}$, C-17), 69.40, 69.57, 69.70 & 69.81($\text{CH}(\text{CH}_3)\text{O}$, C-11,14), 169.76, 170.01 and 170.57 ($\text{C}=\text{O}$). DMAP peaks at (39.67, 106.88 and 147.31).

1.C5: 1,4-Butanediol Initiated Polymerisation of *rac*-Lactide.



Gh17-30 (1,4-butanediol : *rac*-lactide; 1 : 3) ^{13}C NMR (CDCl_3 , 75 MHz) ppm: 17.14 & 17.26(CH_3 , C-5,8), 20.49 & 20.86(CH_3 , C-11), 25.40(CH_2 , C-1), 65.23 & 65.30(CH_2O , C-2), 67.10($\text{CH}(\text{CH}_3)\text{OH}$, C-10), 69.42 & 69.79($\text{CH}(\text{CH}_3)\text{O}$, C-4,7), 169.77 & 170.49($\text{C}=\text{O}$) and 176.07(COOH).

1.C6: Hexadecanol Initiated Polymerisation of Lactide.

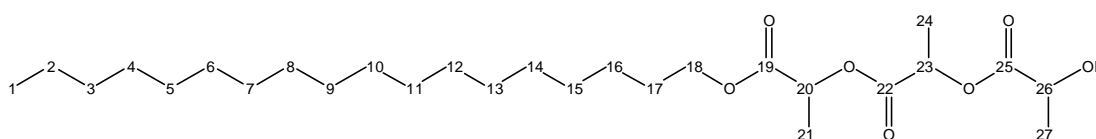


Gh17-38 (Hexadecanol : *rac*-lactide; 1 : 3) ^{13}C NMR (CDCl_3 , 75 MHz) ppm: 14.51(CH_3 , C-1), 17.05, 17.13, 17.21 & 17.30(CH_3 , C-19,22), 20.45, 20.51 & 20.89(CH_3 , C-25), 23.07(CH_2 , C-2), 26.11(CH_2 , C-14), 28.83 & 28.92(CH_2 , C-4,13,15), 29.56, 29.74, 29.87, 29.94 & 30.07(CH_2 , C-5-12), 32.30(CH_2 , C-3), 66.09 & 66.18(CH_2O , C-16), 67.01 & 67.08($\text{CH}(\text{CH}_3)\text{O}$, C-24), 69.40, 69.56, 69.70 &

69.80(CH(CH₃)O, C-18,21), 169.75 & 170.00(C=O). DMAP peaks at (39.53, 106.90 and 148.55).

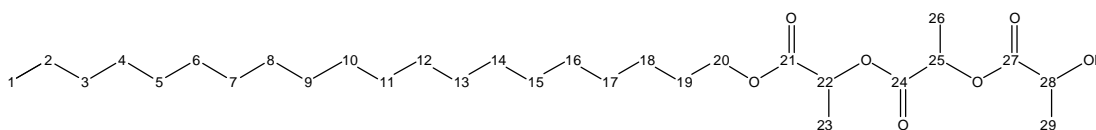
Gh17-41 (Hexadecanol : *rac*-lactide; 1 : 10) ¹³C NMR (CDCl₃, 75 MHz) (important characteristic peaks) ppm: 66.10(CH₂O, C-16), 67.09(CH(CH₃)O, C-24), 69.40, 69.58, 69.70 & 69.81(CH(CH₃)O, C-18,21), 169.77 & 170.02(C=O). DMAP peaks at (39.55, 106.93 and 148.81).

1.C7: Octadecanol Initiated Polymerisation of *rac*-Lactide.



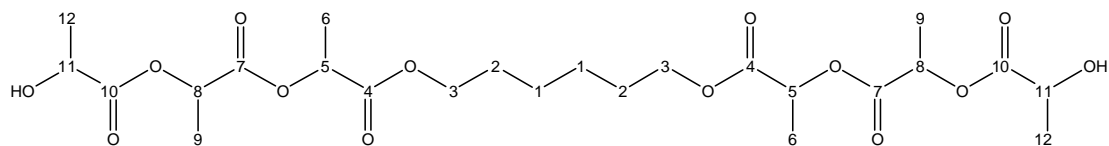
Gh17-39 (Octadecanol : *rac*-lactide; 1 : 3) ¹³C NMR (CDCl₃, 75 MHz) ppm: 14.52(CH₃, C-1), 17.06 & 17.14(CH₃, C-21,24), 20.90(CH₃, C-27), 23.09(CH₂, C-2), 26.13(CH₂, C-16), 28.84 (CH₂, C-4,15,17), 29.57, 29.75, 29.88, 29.95 & 30.08(CH₂, C-5-14), 32.31(CH₂, C-3), 66.10 & 66.22(CH₂O, C-18), 67.10(CH(CH₃)OH, C-26), 69.42, 69.58, 69.70 & 69.81(CH(CH₃)O, C-20,23), 169.75 & 170.00(C=O). DMAP peaks at (39.53, 106.90 and 148.55).

1.C8: Eicosanol Initiated Polymerisation of *rac*-Lactide.



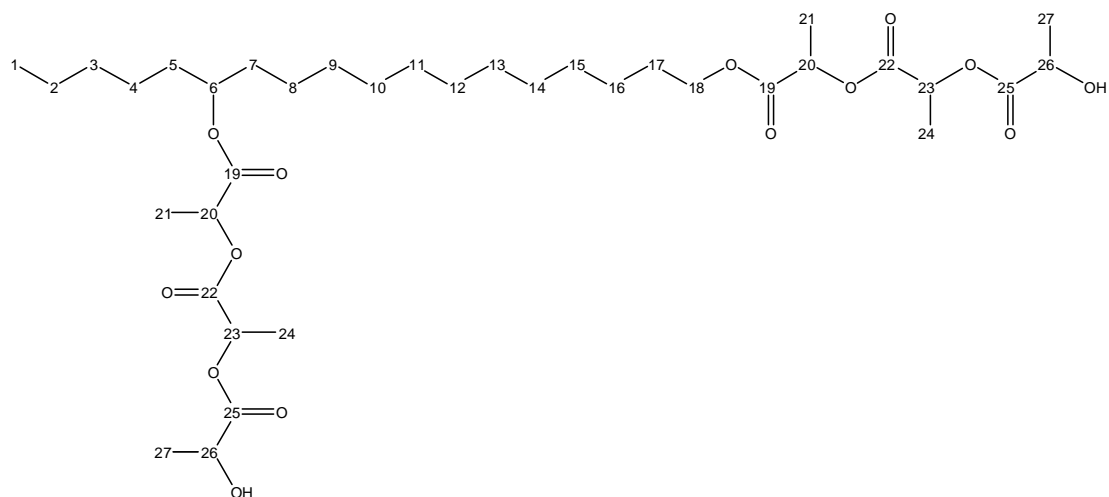
Gh17-40 (Eicosanol : *rac*-lactide; 1 : 3) ¹³C NMR (CDCl₃, 75 MHz) ppm: 14.52(CH₃, C-1), 17.07 & 17.14(CH₃, C-23,26), 20.91(CH₃, C-29), 23.09(CH₂, C-2), 26.13(CH₂, C-18), 28.85 (CH₂, C-4,17,19), 29.58, 29.76, 29.89, 29.96 & 30.09(CH₂, C-5-16), 32.32(CH₂, C-3), 66.10(CH₂O, C-20), 67.10(CH(CH₃)OH, C-28), 69.42, 69.58, 69.70 & 69.82(CH(CH₃)O, C-22,25). DMAP peaks at (39.63 and 106.91).

1.C9: 1,6-Hexanediol Initiated Polymerisation of *rac*-Lactide.



Gh17-43 (1,6-hexanediol : *rac*-lactide; 1 : 3) ^{13}C NMR(CDCl_3 , 75 MHz) ppm: 17.07, 17.14 & 17.29(CH_3 , C-6,9), 20.45, 20.52 & 20.86(CH_3 , C-12), 25.71(CH_2 , C-1), 28.71(CH_2 , C-2), 65.79(CH_2O , C-3), 67.10($\text{CH}(\text{CH}_3)\text{OH}$, C-11), 69.42, 69.55 & 69.77($\text{CH}(\text{CH}_3)\text{O}$, C-5,8), 169.75, 170.57 & 170.72($\text{C}=\text{O}$), 175.32, 175.49 and 176.17(COOH).

1.C10: 1,12-Octadecanediol Initiated Polymerisation of *rac*-Lactide.

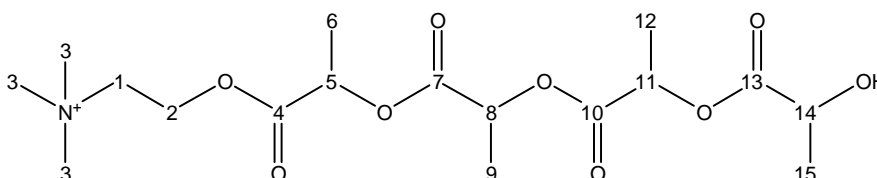


Gh17-44 (1,12-octadecanediol : *rac*-lactide; 1 : 6) ^{13}C NMR(CDCl_3 , 75 MHz) ppm: 17.05 & 17.15 (CH_3 , C-21,24), 20.46 & 20.92(CH_3 , C-27), 24.25(CH_2 , C-4,8), 26.13(CH_2 , C-16), 29.57, 29.89 & 30.10(CH_2 , C-9-15), 32.09(CH_2 , C-3), 66.09(CH_2O , C-18), 67.10($\text{CH}(\text{CH}_3)\text{OH}$, C-26), 69.41, 69.58, 69.71 & 69.83($\text{CH}(\text{CH}_3)\text{O}$, C-20,23) and 169.65($\text{C}=\text{O}$). DMAP peaks at (39.62, 106.92 and 148.24).

Appendix 2: ^{13}C NMR assignments of Poly(lactic acid) Polymers initiated by Polar molecules.

A. Choline Chloride Initiated Polymers.

2.A1: Choline Chloride Initiated Polymerisation of *rac*-Lactide in $^t\text{Butanol}$.



Gh17-ChoPLA001 (choline chloride : *rac*-lactide 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz)
 $\delta(\text{ppm})$: 15.78(lactide), 16.78, 17.09(CH_3 , C-6,9,13), 20.27 & 20.46(CH_3 , C-15), 54.25 & 54.53 (N^+-CH_3 , C-3), 56.19(CH_2-O , C-2), 64.59(CH_2-N^+ , C-1), 66.93($\text{CH}(\text{CH}_3)\text{OH}$, C-14), 68.95, 69.35, 70.44($\text{CH}(\text{CH}_3)\text{O}$, C-5,8,11), 173.27 & 173.89($\text{C}=\text{O}$) and 175.05 (COOH , water initiated polymerisation).

Gh17-ChoPLA002 (choline chloride : *rac*-lactide 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz)
 $\delta(\text{ppm})$: 15.74(lactide), 16.38, 16.67, 16-74, 16.82, 16.86 & 16.99(CH_3 , C-6,9,13), 20.05, 20.21 & 20.40(CH_3 , C-15), 54.24 & 54.48 (N^+-CH_3 , C-3), 56.22 & 59.23(CH_2-O , C-2), 64.59(CH_2-N^+ , C-1), 66.62, 66.69 & 66.91($\text{CH}(\text{CH}_3)\text{OH}$, C-14), 68.97, 69.04, 69.28, 69.97, 70.09($\text{CH}(\text{CH}_3)\text{O}$, C-5,8,11), 72.52(lactide), 169.45, 169.54, 169.65 & 169.77($\text{C}=\text{O}$), 173.18 & 173.76($\text{C}=\text{O}$) and 174.93 & 175.00 (COOH , water initiated polymerisation).

Additional: 31.07(CH_3-C , $^t\text{butanol}$) and 67.91($\text{C}-\text{OH}$, $^t\text{butanol}$).

Gh17-ChoPLA003 (choline chloride : *rac*-lactide 1 : 20) ^{13}C NMR (CDCl_3 , 75 MHz)
 $\delta(\text{ppm})$: 15.70(lactide), 16.40, 16.71, 17.27 & 17.55(CH_3 , C-6,9,13), 20.46(CH_3 , C-15), 54.23(N^+-CH_3 , C-3), 59.13(CH_2-O , C-2), 64.59(CH_2-N^+ , C-1), 66.62($\text{CH}(\text{CH}_3)\text{OH}$, C-14), 68.99, 69.16 & 69.41($\text{CH}(\text{CH}_3)\text{O}$, C-5,8,11), 72.50 (lactide) 167.68, 169.34, 169.42, 169.58 & 169.76($\text{C}=\text{O}$).

Additional: 31.17(CH_3-C , $^t\text{butanol}$), 72.89(unreacted lactide)

Gh17-ChoPLA004 (choline chloride : *rac*-lactide 1 : 15) ^{13}C NMR (CDCl_3 , 75 MHz)
 δ (ppm): 16.15, 16.80, 17.09 & 17.13(CH_3 , C-6,9,13), 20.91(CH_3 , C-15), 54.66(N^+ - CH_3 , C-3), ~59.13(CH_2 -O, C-2), ~64.59(CH_2 - N^+ , C-1), 67.03($\text{CH}(\text{CH}_3)\text{OH}$, C-14), 69.39 & 69.57($\text{CH}(\text{CH}_3)\text{O}$, C-5,8,11) and 169.76 & 170.00($\text{C}=\text{O}$).

Additional: 31.61(CH_3 -C, t butanol), 72.90(unreacted lactide).

Gh17-ChoPla006a (choline chloride : *rac*-lactide 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz)
 δ (ppm): 16.11, 16.82, 17.04, 17.14, 17.87 & 18.00(CH_3 , C-6,9,12), 20.71 & 20.89(CH_3 , C-15), 54.56 & 54.93 (N^+ - CH_3 , C-3), 56.55 & 59.57(CH_2 -O, C-2), 64.85(N^+ - CH_2 , C-1), 66.99 & 67.48($\text{CH}(\text{CH}_3)\text{OH}$, C-14), 69.39, 69.92 & 72.06 ($\text{CH}(\text{CH}_3)\text{O}$, C-5,8,11), 72.25(lactide?), 72.93(?), 157.21(??) and 169.80, 169.98 & 170.17($\text{C}=\text{O}$)

Gh17-ChoPla006b (choline chloride : *rac*-lactide 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz)
 δ (ppm): 15.75(lactide), 16.44, 16.66, 16.75, 17.50(CH_3 , C-6,9,12), 20.35 & 20.51(CH_3 , C-15), 27.91(??), 54.19 & 54.56(N^+ - CH_3 , C-3), 56.16 & 59.19(CH_2 -O, C-2), 64.49(N^+ - CH_2 , C-1), 66.62 & 67.05($\text{CH}(\text{CH}_3)\text{OH}$, C-14), 68.11(??), 69.00, 69.52 & 71.62($\text{CH}(\text{CH}_3)\text{O}$, C-5,8,11), 72.53(lactide), 156.92(lactoyl lactate ?), 169.41 & 169.59($\text{C}=\text{O}$) and 174.60 & 175.09(COOH).

Gh17-ChoPla007 (choline chloride : *rac*-lactide 1 : 3) ^{13}C NMR (CDCl_3 , 75 MHz)
 δ (ppm): 15.76(lactide), 16.43, 16.67 & 17.77(CH_3 , C-6,9,12), 20.36 & 20.54(CH_3 , C-15), 54.18 & 54.57(CH_3 - N^+ , C-3), 56.09 & 59.15(CH_2O , C-2), 64.47(CH_2 - N^+ , C-1), 66.56 67.12 & 68.12($\text{CH}(\text{CH}_3)\text{OH}$, C-14), 68.63(t Butyl Ester), 69.00 & 69.63($\text{CH}(\text{CH}_3)\text{O}$, C-5,8,11), 72.54(lactide) and 169.42($\text{C}=\text{O}$)

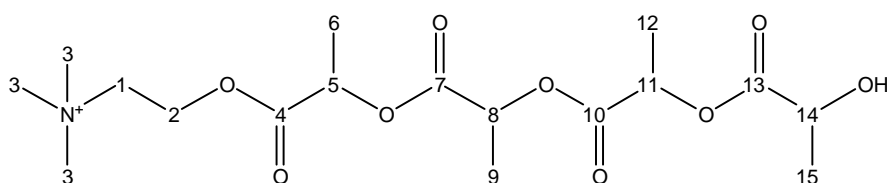
Gh17-ChoLPLA001 (choline chloride : L-lactide 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz)
 δ (ppm): 15.74(lactide), 16.44, 16.64 & 17.59(CH_3 , C-6,9,12), 20.52(CH_3 , C-15), 54.27 & 54.65(CH_3 - N^+ , C-3), 59.14(CH_2O , C-2), 64.56(CH_2 - N^+ , C-1), 66.60($\text{CH}(\text{CH}_3)\text{OH}$, C-14), 68.71, 69.00 & 69.62($\text{CH}(\text{CH}_3)\text{O}$, C-5,8,11), 72.54(lactide), 72.90(? – possibly lactoyl lactate) 167.64(lactide), 169.40 and 169.58($\text{C}=\text{O}$).

Gh17-ChoPLA(B003.1) (choline chloride : *rac*-lactide, 1 : 15) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.70(lactide), 16.44, 16.63 & 17.56(CH_3 , C-6,9,12), 20.45(CH_3 , C-15), 54.25($\text{CH}_3\text{-N}^+$, C-3), 59.22(CH_2O , C-2), 64.59($\text{CH}_2\text{-N}^+$, C-1), 66.56($\text{CH}(\text{CH}_3)\text{OH}$, C-14), 68.99($\text{CH}(\text{CH}_3)\text{O}$, C-5,8,11), 72.53(lactide), 72.90(lactide), and 169.42 & 169.59($\text{C}=\text{O}$).

Gh17-ChoLPLA(B006) (choline chloride : L-lactide, 1 : 15) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.76(lactide), 16.42, 16.64, 16.74 & 17.59(CH_3 , C-6,9,12), 20.28 & 20.47(CH_3 , C-15), 54.35 ($\text{CH}_3\text{-N}^+$, C-3), 59.18(CH_2O , C-2), 64.65($\text{CH}_2\text{-N}^+$, C-1), 66.68 & 66.81($\text{CH}(\text{CH}_3)\text{OH}$, C-14), 68.85, 69.02, 69.22, 69.65 & 69.74($\text{CH}(\text{CH}_3)\text{O}$, C-5,8,11), 72.51(lactide), 72.91(lactoyl lactate), 167.55(lactide), 169.60, 169.72 & 169.84 ($\text{C}=\text{O}$) and 175.16(COOH).

Gh17-ChoPLA(B007) (choline chloride : *rac*-lactide, 1 : 15) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.78(lactide), 16.66 & 17.17(CH_3 , C-6,9,12), 20.49(CH_3 , C-15), 54.32($\text{CH}_3\text{-N}^+$, C-3), 64.58($\text{CH}_2\text{-N}^+$, C-1), 69.02 & 69.48($\text{CH}(\text{CH}_3)\text{O}$, C-5,8,11), 72.50(lactide), 167.47(lactide) and 169.47 & 169.56($\text{C}=\text{O}$).

2.A2: Choline Chloride Initiated Polymerisation of *rac*-Lactide in a melt reaction from a Eutectic Mixture.



Gh17-132 (Choline chloride/Citric Acid : *rac*-lactide 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.03(lactide), 16.29, 16.44, 16.51, 16.59, 16.65 & 16.98(CH_3 , C-6,9,12), 20.30(CH_3 , C-15), 42.74($\text{CH}_2\text{-C-O}$, citric acid), 52.85(CH_3N^+ , C-3), 58.76 & 58.92 ($\text{CH}_2\text{-O}$, C-2), 65.41 & 65.52 ($\text{CH}_2\text{-N}^+$, C-1), 67.73($\text{CH}(\text{CH}_3)\text{OH}$, C-14), 68.05, 68.21, 68.52, 68.71, 68.93 & 69.10($\text{CH}(\text{CH}_3)\text{O}$, C-5,8,11), 72.14(??), 168.49 and ~169($\text{C}=\text{O}$, PLA), 171.22 and ~174(COOH , citric acid).

Gh17-ChoPlaEut4 (Choline chloride/urea : *rac*-lactide 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz) $\delta(\text{ppm})$: 15.66(lactide), 16.41, 16.63, 17.15 & 17.54(CH_3 , C-6,9,12), 20.46(CH_3 , C-15), 54.16 & 54.42(CH_3 , C-3), 59.15($\text{CH}_2\text{-O}$, C-2), 64.55($\text{CH}_2\text{-N}^+$, C-1), 66.51($\text{CH}(\text{CH}_3)\text{OH}$, C-14), 68.97($\text{CH}(\text{CH}_3)\text{O}$, C-5,8,11), 72.55(lactide), 161.65(Urea), 167.87(lactide), 169.39 & 169.56($\text{C}=\text{O}$), 175.01(COOH).

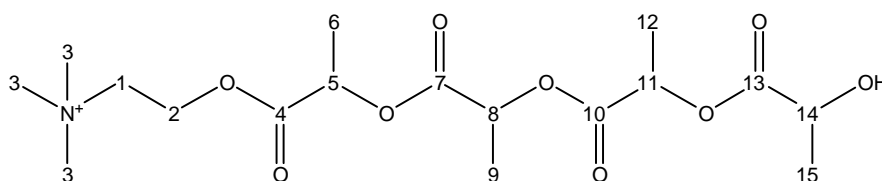
Gh17-ChoPlaUrea001 (Choline chloride/urea : *rac*-lactide 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) $\delta(\text{ppm})$: 15.77 (lactide), 16.49, 16.67 & 17.61(CH_3 , C-6,9,12), 20.52(CH_3 , C-15), 54.32 (CH_3 , C-3), 59.14($\text{CH}_2\text{-O}$, C-2), 64.61($\text{CH}_2\text{-N}^+$, C-1), 66.67($\text{CH}(\text{CH}_3)\text{OH}$, C-14), 69.02($\text{CH}(\text{CH}_3)\text{O}$, C-5,8,11), 72.53(lactide), 167.59(lactide) and 169.38 & 169.56($\text{C}=\text{O}$)

Gh17-ChoPLAUrea002 (Choline chloride/urea : *rac*-lactide 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) $\delta(\text{ppm})$: 15.79 (lactide), 16.48, 16.67 & 17.61(CH_3 , C-6,9,12), 20.51(CH_3 , C-15), 54.33 (CH_3 , C-3), 59.16($\text{CH}_2\text{-O}$, C-2), 64.63($\text{CH}_2\text{-N}^+$, C-1), 66.69($\text{CH}(\text{CH}_3)\text{OH}$, C-14), 69.02($\text{CH}(\text{CH}_3)\text{O}$, C-5,8,11), 72.53(lactide), and 169.38 & 169.62($\text{C}=\text{O}$).

Gh17-ChoPLAUrea003 (Choline chloride/urea : *rac*-lactide 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) $\delta(\text{ppm})$: 15.75 (lactide), 16.43, 16.66, 17.09 & 17.59(CH_3 , C-6,9,12), 20.13 & 20.48(CH_3 , C-15), 54.25 (CH_3 , C-3), 59.16($\text{CH}_2\text{-O}$, C-2), 64.62($\text{CH}_2\text{-N}^+$, C-1), 66.62($\text{CH}(\text{CH}_3)\text{OH}$, C-14), 69.02 & 69.78($\text{CH}(\text{CH}_3)\text{O}$, C-5,8,11), 72.54(lactide), 161.5 (urea) and 169.44 & 169.60($\text{C}=\text{O}$).

Gh17-ChoPLAUrea004 (Choline chloride/urea : *rac*-lactide 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) $\delta(\text{ppm})$: 15.77 (lactide), 16.66, & 17.61(CH_3 , C-6,9,12), 20.51(CH_3 , C-15), 54.36(CH_3 , C-3), 59.15($\text{CH}_2\text{-O}$, C-2), 64.67($\text{CH}_2\text{-N}^+$, C-1), 66.67($\text{CH}(\text{CH}_3)\text{OH}$, C-14), 69.02($\text{CH}(\text{CH}_3)\text{O}$, C-5,8,11), 72.53(lactide), and 169.37 & 169.62($\text{C}=\text{O}$).

2.A3: Choline Chloride Initiated polymerisations of *rac*-Lactide in a melt using Sn(oct)₂ as catalyst.



Gh17-ChoPla009 (Choline Chloride : *rac*-lactide 1 : 10) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 15.80(lactide), 16.40, 16.66 & 17.62(CH₃, C-6,9,12), 20.53(CH₃, C-15), 54.40(CH₃-N⁺, C-3), 59.07(CH₂-O, C-2), ~63(CH₂-N⁺, C-1) 66.65(CH(CH₃)OH, C-14), 69.01(CH(CH₃)O, C-5,8,11) 72.50(lactide), 72.9(?) and 169.35(C=O).

Gh17-ChoPla010 (Choline Chloride : *rac*-lactide 1 : 20) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 16.13, 17.04 & 17.96(CH₃, C-6,9,12), 20.89(CH₃, C-15), 54.75(CH₃, C-3), ~59(CH₂O, C-2), ~63(CH₂-N⁺, C-1), ~ 67(CH(CH₃)OH, C-14), 69.38, 69.79(CH(CH₃)O, C-5,8,11), 72.89(?), 73.29(???), 168, 169.76 and 170(C=O)

Gh17-ChoPla011a (15 mins) (Choline Chloride : *rac*-lactide 1 : 20) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 15.67(lactide), 16.38, 16.62 & 17.51(CH₃, C-6,9,12), 20.46(CH₃, C-15), 54.30(CH₃, C-3), 59.04(CH₂-O, C-2), 64.63(CH₂-N⁺, C-1), ~67(CH(CH₃)OH, C-14), 68.98(CH(CH₃)O, C-5,8,11), 72.49(lactide), 72.89(?), 167.74(C=O, lactide) and 169.34, 169.43 & 169.57(C=O).

Gh17-ChoPla011b (30 mins) (Choline Chloride : *rac*-lactide 1 : 20) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 15.61(lactide), 16.36, 16.60 & 17.45(CH₃, C-6,9,12), 20.42(CH₃, C-15), 54.25(CH₃, C-3), ~59(CH₂-O, C-2), ~64(CH₂-N⁺, C-1), ~67(CH(CH₃)OH, C-14), 68.97(CH(CH₃)O, C-5,8,11) 72.47(lactide), 72.88(?), 167.83(C=O, lactide) and ~169(C=O).

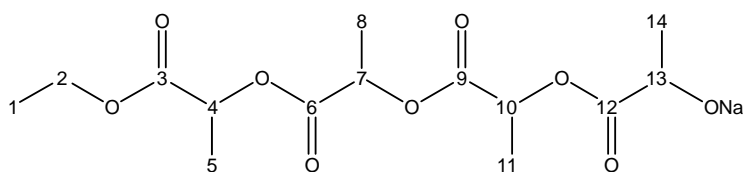
Gh17-ChoPla011c (60 mins) (Choline Chloride : *rac*-lactide 1 : 20) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 15.77(lactide), 16.41, 16.65 & 17.60(CH₃, C-6,9,12), 20.51(CH₃, C-15), 54.38(CH₃, C-3), 59.09(CH₂-O, C-2), 64.64(CH₂-N⁺, C-1),

66.66(CH(CH₃)OH, C-14), 69.00(CH(CH₃)O, C-5,8,11) 72.50(lactide), 72.90(?), 167.52(C=O, lactide), 169.37 and 169.61(C=O).

Gh17-ChoPla012 (Choline Chloride : *rac*-lactide 1 : 20) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 15.75(lactide), 16.67, & 17.57(CH₃, C-6,9,12), ~20.5(CH₃, C-15), 54.38(CH₃, C-3), ~59(CH₂-O, C-2), ~64.64(CH₂-N⁺, C-1), 67.95(THF) 69.02(CH(CH₃)O, C-5,8,11), 72.49(lactide), 72.91(?), 167.52(C=O, lactide), ~169(C=O).

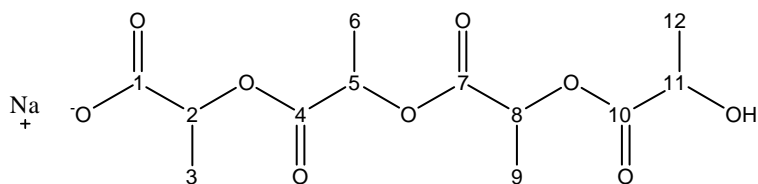
B. Sodium/Potassium Hydroxycarboxylate Initiated Polymers.

2.B1: Sodium Acetate Initiated Polymers



Gh17-EtPLANa001 (Sodium acetate : ethanol : *rac*-lactide; 1 : 2 : 6) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 14.05(CH₃, C-1), 15.80(lactide), 16.65, 17.22 & 17.62(CH₃, C-5,8,11), 20.05 & 20.51(CH₃, C-12), 61.55(CH₂-O, C-2), 66.70(CH(CH₃)OH, C-11), 69.01, 69.18, 69.32 & 69.43(CH(CH₃)O, C-2,5,8), 72.47 (CH(CH₃)ONa), 169.36 and 169.61(C=O).

2.B2: Sodium Lactate Initiated Polymers.



Gh17-NaPLA001 (Sodium lactate : *rac*-lactide; 1 : 6) ¹³C NMR (CDCl₃, 75 MHz)
δ(ppm): 16.20, 17.04 & 17.62(CH₃, C-6,9), 18.01(CH₃, C-3), 20.90(CH₃, C-12),
67.21(CH(CH₃)OH, C-11), 69.40 & 69.58(CH(CH₃)O, C-2,5,8), 72.87(?), 169.78 and
170.04(C=O).

Gh17-NaPLA003 (Sodium lactate : *rac*-lactide;) ¹³C NMR (CDCl₃, 75 MHz)
δ(ppm): 15.82(lactide), 16.65, 17.22 & 17.62(CH₃, C-3,6,9), 20.90(CH₃, C-12),
67.98(CH(CH₃)OH, C-11), 69.01 & 69.19(CH(CH₃)O, C-2,5,8), 72.47(lactide),
169.37 and 169.62(C=O).

Gh17-NaPLA004 (Sodium lactate : *rac*-lactide;) ¹³C NMR (CDCl₃, 75 MHz)
δ(ppm): 15.79(lactide), 16.64, 16.73, 17.16 & 17.60(CH₃, C-3,6,9), 20.48(CH₃, C-
12), 66.63(CH(CH₃)OH, C-11), 69.00, 69.18 & 69.43(CH(CH₃)O, C-2,5,8), 72.47
(lactide), 72.90(lactide), 167.41(C=O, lactide) 169.41, 169.37, 169.62 and
170.17(C=O).

Gh17-NaLPLA001 (Sodium lactate : L-lactide; 1 : 6) ¹³C NMR (CDCl₃, 75 MHz)
δ(ppm): 15.82(lactide), 16.64 & 17.14(CH₃, C-3,6,9), 20.50(CH₃, C-12),
66.66(CH(CH₃)OH, C-11), 69.01 & 69.66(CH(CH₃)O, C-2,5,8), 72.47(lactide) and
169.61(C=O).

Gh17-NaLPLA002 (Sodium lactate : L-lactide; 1 : 12) ¹³C NMR (CDCl₃, 75 MHz)
δ(ppm): 15.82(lactide), 16.64 & 17.06(CH₃, C-3,6,9), 20.50(CH₃, C-12),
66.67(CH(CH₃)OH, C-11), 69.01(CH(CH₃)O, C-2,5,8), 72.47(lactide) and
169.62(C=O).

Gh17-NaLPLA003 (Sodium lactate : L-lactide; 1 : 20) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.82(lactide), 16.64 & 17.62(CH_3 , C-3,6,9), 20.50(CH_3 , C-12), 66.88($\text{CH}(\text{CH}_3)\text{OH}$, C-11), 69.01($\text{CH}(\text{CH}_3)\text{O}$, C-2,5,8), 72.47(lactide), 72.91(?) and 169.62($\text{C}=\text{O}$).

Gh17-NaPLA(B002) (Sodium lactate : *rac*-lactide; 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 16.15, 17.03, 17.12, 17.49 & 17.97(CH_3 , C-3,6,9), 20.86(CH_3 , C-12), 66.99($\text{CH}(\text{CH}_3)\text{OH}$, C-11), 69.39, 69.57, & 69.81($\text{CH}(\text{CH}_3)\text{O}$, C-2,5,8), 72.85(lactide), 73.29(?), 167.90(lactide) and 169.57, 169.77 & 170.01($\text{C}=\text{O}$).

Gh17-NaPLA(B002.1) (Sodium lactate : *rac*-lactide; 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.80(lactide), 16.65, 16.74, 17.20 & 17.61(CH_3 , C-3,6,9), 20.50(CH_3 , C-12), 66.64($\text{CH}(\text{CH}_3)\text{OH}$, C-11), 69.00, 69.18, & 69.43($\text{CH}(\text{CH}_3)\text{O}$, C-2,5,8), 72.46(lactide), 72.85(?), 167.38(lactide) and 169.16, 169.37 & 169.63($\text{C}=\text{O}$).

Gh17-NaPLA(B002.11) (Sodium lactate : *rac*-lactide; 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.83(lactide), 16.67, 16.76 & 17.20(CH_3 , C-3,6,9), 20.53(CH_3 , C-12), 69.02, 69.20, & 69.44($\text{CH}(\text{CH}_3)\text{O}$, C-2,5,8), 72.48($\text{CH}(\text{CH}_3)\text{ONa}$), 72.85(lactide ?) and 169.38 & 169.63($\text{C}=\text{O}$).

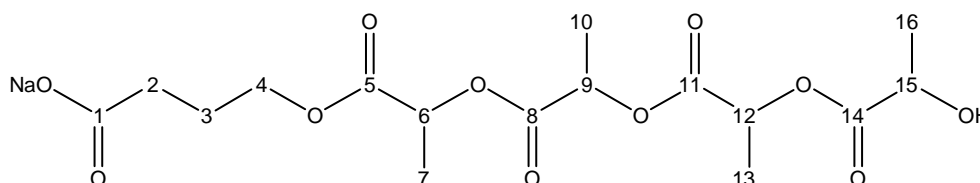
Gh17-NaPLA(B002.2) (Sodium lactate : *rac*-lactide; 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.82(lactide), 16.65, 77.28(CH_3 , C-3,6,9), 20.50(CH_3 , C-12), 69.02, & 69.19($\text{CH}(\text{CH}_3)\text{O}$, C-2,5,8), 169.37 & 169.61($\text{C}=\text{O}$).

Gh17-NaLPLA(B004.1) (Sodium lactate : L-lactide; 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.82(lactide), 16.65 & 17.04(CH_3 , C-3,6,9), 20.51(CH_3 , C-12), 66.67($\text{CH}(\text{CH}_3)\text{OH}$, C-11), 69.00 & 69.45($\text{CH}(\text{CH}_3)\text{O}$, C-2,5,8), 72.47(lactide) and 169.62($\text{C}=\text{O}$).

Gh17-NaLPLA(B004.11) (Sodium lactate : L-lactide; 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.83(lactide), 16.66 & 17.11(CH_3 , C-3,6,9), ~20.5(CH_3 , C-12), ~66.5($\text{CH}(\text{CH}_3)\text{OH}$, C-11), 69.02 & 69.45($\text{CH}(\text{CH}_3)\text{O}$, C-2,5,8), and 169.38 & 169.63($\text{C}=\text{O}$).

Gh17-NaLPLA(B004.2) (Sodium lactate : L-lactide; 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 17.03(CH_3 , C-3,6,9), 69.40($\text{CH}(\text{CH}_3)\text{O}$, C-2,5,8) and 170.00($\text{C}=\text{O}$).

2.B3: Sodium γ -Hydroxybutyrate Initiated Polymers.



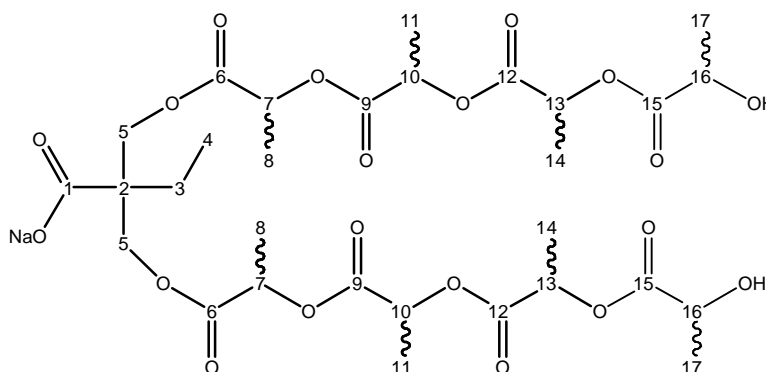
Gh17-NaButPLA001 (Sodium hydroxybutyrate : *rac*-lactide; 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.82(lactide), 16.65 & 17.23(CH_3 , C-7,10,13), 20.49(CH_3 , C-16), 66.16($\text{CH}(\text{CH}_3)\text{OH}$, C-15), 69.01, 69.19 & 69.45($\text{CH}(\text{CH}_3)\text{O}$, C-6,9,12) and 169.38 & 169.63($\text{C}=\text{O}$).

Gh17-NaButLPLA (Sodium hydroxybutyrate : L-lactide; 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.81(lactide), 16.64 & 17.25(CH_3 , C-7,10,13), 20.50(CH_3 , C-16), 22.19(CH_2 , C-3), 24.38(CH_2 , C-2), 65.05($\text{CH}_2\text{-O}$, C-4), 66.63($\text{CH}(\text{CH}_3)\text{OH}$, C-15), 69.01, & 69.44($\text{CH}(\text{CH}_3)\text{O}$, C-6,9,12) and 169.61 & 170.50($\text{C}=\text{O}$).

Gh17-NaButLPLA (Sodium hydroxybutyrate : L-lactide; 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.82(lactide), 16.65, 16.75(CH_3 , C-7,10,13), 20.52(CH_3 , C-16), ~23.8(CH_2 , C-3), ~65($\text{CH}_2\text{-O}$, C-4), ~67($\text{CH}(\text{CH}_3)\text{OH}$, C-15), 69.01, 69.34 & 69.44($\text{CH}(\text{CH}_3)\text{O}$, C-6,9,12), 72.47(lactide) and 169.63($\text{C}=\text{O}$).

Gh17-NaGHBuAPLA001 (Sodium hydroxybutyrate : *rac*-lactide; 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.77(lactide), 16.65, 16.74 & 17.24(CH_3 , C-7,10,13), 20.07 & 20.49(CH_3 , C-16), 22.19(CH_2 , C-3), 27.79(CH_2 , C-2), 66.61($\text{CH}(\text{CH}_3)\text{OH}$, C-15), 68.51($\text{CH}_2\text{-O}$, C-4), 69.00, 69.18 & 69.42($\text{CH}(\text{CH}_3)\text{O}$, C-6,9,12), 72.47(lactide) and 169.35 & 169.61($\text{C}=\text{O}$).

2.B4: Sodium Bis(hydroxymethyl)butyrate Initiated Polymers.



Gh17-BHBPLA001 (2,2-bis(hydroxymethyl)butyrate : *rac*-lactide; 1 : 12; Sn-oct) ^{13}C NMR (CDCl_3 , 75 MHz) $\delta(\text{ppm})$:): 8.44(CH_3 , C-4), 16.18, 17.05 & 17.11(CH_3 , C-8, 11, 14), 20.86(CH_3 , C-14), 67.10($\text{CH}(\text{CH}_3)\text{OH}$, C-16), 69.40 & 69.58($\text{CH}(\text{CH}_3)\text{O}$, C-7, 10, 13) and 169.61, 169.76 & 170.00($\text{C}=\text{O}$).

Gh17-NaBHBPLA001 (Sodium bis(hydroxymethyl)butyrate : *rac*-lactide; 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) $\delta(\text{ppm})$: 15.82(lactide), 16.66(CH_3 , C-8, 11, 14), 69.01, 69.19 & 69.47($\text{CH}(\text{CH}_3)\text{O}$, C-7, 10, 13), 169.37($\text{C}=\text{O}$).

Gh17-NaBHBPLA002 (Sodium bis(hydroxymethyl)butyrate : *rac*-lactide; 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz) $\delta(\text{ppm})$: 8.41(CH_3 , C-4), 16.67(CH_3 , C-8, 11, 14), 20.06 & 20.51(CH_3 , C-14), 24.01(CH_2 , C-3), 66.66($\text{CH}(\text{CH}_3)\text{OH}$, C-16), 69.03, 69.20 & 69.93($\text{CH}(\text{CH}_3)\text{O}$, C-7, 10, 13) and 169.38($\text{C}=\text{O}$).

Gh17-NaBHBPLA003 (Sodium bis(hydroxymethyl)butyrate : *rac*-lactide; 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) $\delta(\text{ppm})$: 8.32(CH_3 , C-4), 15.81(lactide), 16.65 & 16.75(CH_3 , C-8, 11, 14), 20.06 & 20.51(CH_3 , C-14), 66.64($\text{CH}(\text{CH}_3)\text{OH}$, C-16), 69.01, 69.19 & 69.43($\text{CH}(\text{CH}_3)\text{O}$, C-7, 10, 13), 72.47(lactide) and 169.16, 169.37 & 169.62($\text{C}=\text{O}$).

Gh17-NaBHBPLAB006 (Sodium bis(hydroxymethyl)butyrate : *rac*-lactide; 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) $\delta(\text{ppm})$: 16.67(CH_3 , C-8, 11, 14), 20.53(CH_3 , C-14), 66.63($\text{CH}(\text{CH}_3)\text{OH}$, C-16), 69.03 & 69.21($\text{CH}(\text{CH}_3)\text{O}$, C-7, 10, 13) and 169.38 & 169.65($\text{C}=\text{O}$).

Gh17-NaBHBLPLA001 (Sodium bis(hydroxymethyl)butyrate : L-lactide; 1 : 12) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 15.23(CH₃ ?), 15.82(lactide), 16.64 & 16.73(CH₃, C-8, 11, 14), 20.50(CH₃, C-14), 23.72(CH₂, C-3), 66.71(CH(CH₃)OH, C-16), 69.02 & 69.27(CH(CH₃)O, C-7, 10, 13) and 169.47 & 169.62(C=O).

Gh17-NaBHBLPLA002 (Sodium bis(hydroxymethyl)butyrate : L-lactide; 1 : 6) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 8.36(CH₃, C-4), 15.82(lactide), 16.54(CH₃, C-8, 11, 14), 20.50(CH₃, C-14), 25.61(CH₂, C-3), 66.64(CH(CH₃)OH, C-16), 67.98(CH₂O, C-5), 69.02(CH(CH₃)O, C-7, 10, 13), 169.61(C=O).

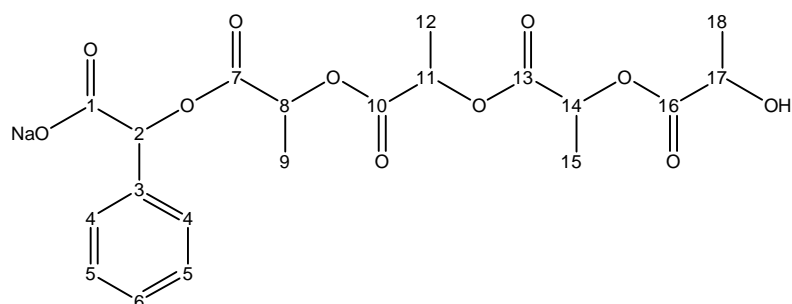
Gh17-NaBHBLPLA003 (Sodium bis(hydroxymethyl)butyrate : L-lactide; 1 : 3) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 8.48(CH₃, C-4), 17.02 & 17.11(CH₃, C-8, 11, 14), 20.48, 20.73 & 20.84(CH₃, C-14), 24.13 & 25.98(CH₂, C-3), 51.16(C-2), 67.10(CH(CH₃)OH, C-16), 68.34(CH₂O, C-5), 69.42 & 69.97(CH(CH₃)O, C-7, 10, 13), 170.00(C=O) and 175.57(COOH).

Gh17-KBHBLPLA001 (Potassium bis(hydroxymethyl)butyrate : L-lactide; 1 : 6) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 17.04(CH₃, C-8, 11, 14), 69.40(CH(CH₃)O, C-7, 10, 13), 72.86(lactoyl lactate) and 170.01(C=O).

Mostly free PLA with little initiator uptake.

NaBHBLPLAB007 (Sodium bis(hydroxymethyl)butyrate : L-lactide; 1 : 12) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 8.60(CH₃, C-4), 16.65 & 16.75(CH₃, C-8, 11, 14), 20.50(CH₃, C-14), ~67(CH(CH₃)OH, C-16), 69.01 & 69.45(CH(CH₃)O, C-7, 10, 13), ~72.4(lactide) and 169.61(C=O).

2.B5: Sodium Mandelate Initiated Polymers.



Gh17-NaMandelaPLA001 (sodium mandelate : *rac*-lactide; 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.80(lactide), 16.66 & 16.75(CH_3 , C-9,12,15), 20.05 & 20.49(CH_3 , C-18), 66.57($\text{CH}(\text{CH}_3)\text{OH}$, C-17), 69.02, 69.20 & 69.45($\text{CH}(\text{CH}_3)\text{O}$, C-8,11,14), 72.48(lactide), ~79($\text{CH}(\text{C}_6\text{H}_5)\text{O}$, C-2), 127.77(CH , C-6), 128.24(CH , C-4,5) and 169.38 & 169.63($\text{C}=\text{O}$).

Gh17-NaMandelaPLA002 (sodium mandelate : *rac*-lactide; 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.78(lactide), 16.41, 16.66, 16.75 & 17.60(CH_3 , C-9,12,15), 20.48 (CH_3 , C-18), 66.59($\text{CH}(\text{CH}_3)\text{OH}$, C-17), 69.01, 69.20 & 69.44($\text{CH}(\text{CH}_3)\text{O}$, C-8,11,14), 72.47 & 72.91(lactide), ~79($\text{CH}(\text{C}_6\text{H}_5)\text{O}$, C-2), 127.70(CH , C-6), 128.24(CH , C-4,5) and 169.38 & 169.62($\text{C}=\text{O}$).

Gh17-NaMandelaPLAB008 (sodium mandelate : *rac*-lactide; 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.82(lactide), 16.67, 16.75 & 17.63(CH_3 , C-9,12,15), 20.50(CH_3 , C-18), ~67($\text{CH}(\text{CH}_3)\text{OH}$, C-17), 69.03 & 69.21($\text{CH}(\text{CH}_3)\text{O}$, C-8,11,14), 127.78(CH , C-6), 128.31(CH , C-4,5) and 169.38 & 169.63($\text{C}=\text{O}$).

Gh17-NaLMandelaLPLA001 (sodium L-mandelate : L-lactide; 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 16.19, 17.03, 17.13 & 18.00 (CH_3 , C-9,12,15), 20.88(CH_3 , C-18), 67.02($\text{CH}(\text{CH}_3)\text{OH}$, C-17), 69.41 & 70.15($\text{CH}(\text{CH}_3)\text{O}$, C-8,11,14), 72.86(lactide), 73.29(Possibly unreacted mandelic acid), 78.76($\text{CH}(\text{C}_6\text{H}_5)\text{O}$, C-2), 128.25(CH , C-6), 128.64(CH , C-5), 136.57(C , C-3), 167.77(Lactide), 170.00, 170.30 & 170.71($\text{C}=\text{O}$), 173.95(COOH).

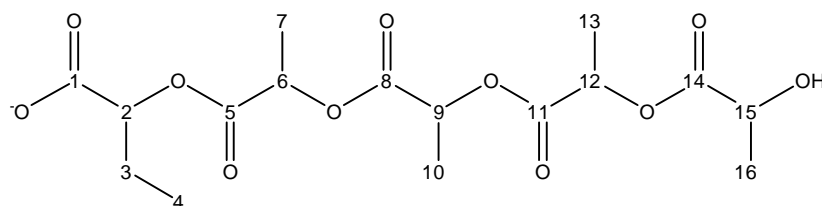
Gh17-NaLMandelaLPLA002 (sodium mandelate : L-lactide; 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.82(lactide), 16.66 & 17.63(CH_3 , C-9,12,15), 20.51(CH_3 , C-18), 66.68($\text{CH}(\text{CH}_3)\text{OH}$, C-17), 69.02, 69.45 & 69.88($\text{CH}(\text{CH}_3)\text{O}$, C-8,11,14), 72.48($\text{CH}(\text{CH}_3)\text{ONa}$, C-17), 72.92(Unreacted lactide or free mandelic acid), 127.92(CH , C-6), 128.32(CH , C-5), 136.07(C , C-3), 169.63, 170.13 & 170.65($\text{C}=\text{O}$), 173.61(COOH).

Gh17-NaMandelaDPLA003 (sodium mandelate : D-lactide; 1 : 20) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.82(lactide), 16.66 & 17.62(CH_3 , C-9,12,15), ~67($\text{CH}(\text{CH}_3)\text{OH}$, C-17), 69.02 & 69.45($\text{CH}(\text{CH}_3)\text{O}$, C-8,11,14), 72.48($\text{CH}(\text{CH}_3)\text{ONa}$, C-17) and 169.63($\text{C}=\text{O}$).

NaMandelaLPLAB012 (sodium mandelate : L-lactide; 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.83(lactide), 16.66 & 17.63(CH_3 , C-9,12,15), 20.52(CH_3 , C-18), ~67($\text{CH}(\text{CH}_3)\text{OH}$, C-17), 69.03($\text{CH}(\text{CH}_3)\text{O}$, C-8,11,14), 72.49($\text{CH}(\text{CH}_3)\text{ONa}$, C-17), 127.91(CH , C-6), 128.36(CH , C-5) and 169.64($\text{C}=\text{O}$).

NaMandelaLPLAB009 (sodium mandelate : L-lactide; 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.83(lactide), 16.66 & 17.63(CH_3 , C-9,12,15), 20.52(CH_3 , C-18), ~67($\text{CH}(\text{CH}_3)\text{OH}$, C-17), 69.03($\text{CH}(\text{CH}_3)\text{O}$, C-8,11,14), 72.49($\text{CH}(\text{CH}_3)\text{ONa}$, C-17), 127.91(CH , C-6), 128.35(CH , C-5) and 169.64($\text{C}=\text{O}$).

2.B6: 2-Hydroxybutyrate Initiated Polymers.

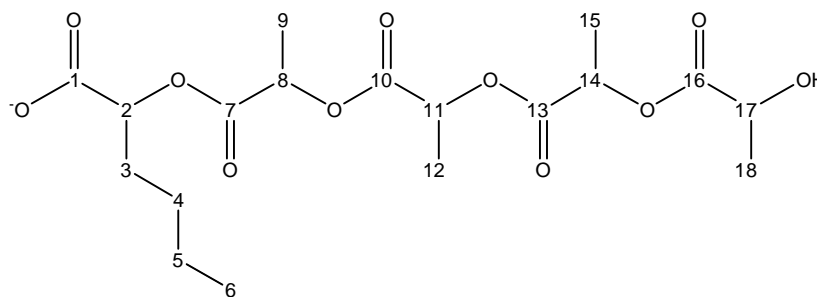


Gh17-NaHBuALPLA001 (Sodium hydroxybutyrate : L-lactide; 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 10.01 & 10.12(CH_3 , C-4), 15.83(lactide), 16.66(CH_3 , C-7, 10, 13), 20.08 & 20.52(CH_3 , C-16), 24.60(CH_2 , C-3), 66.67($\text{CH}(\text{CH}_3)\text{OH}$, C-15), 69.02, 69.45 & 70.09($\text{CH}(\text{CH}_3)\text{O}$, C-6, 9, 12), 72.48(lactide), 77.72($\text{CH}(\text{C}_2\text{H}_5)\text{O}$, C-2), 169.63 & 170.82($\text{C}=\text{O}$, C-5, 8, 11, 14), 175.51(COOH , C-1).

Gh17-NaHBuALPLA002 (Sodium hydroxybutyrate : L-lactide; 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 10.93(CH_3 , C-4), 15.81(lactide), 16.65 & 17.62(CH_3 , C-7, 10, 13), 20.51(CH_3 , C-16), 24.80(CH_2 , C-3), ~67($\text{CH}(\text{CH}_3)\text{OH}$, C-15), 69.01 & 69.45 ($\text{CH}(\text{CH}_3)\text{O}$, C-6, 9, 12), 72.47(lactide), 72.89($\text{CH}(\text{C}_2\text{H}_5)\text{O}$, C-2) and 169.62($\text{C}=\text{O}$).

Gh17-NaHBuAPLA002 (Sodium hydroxybutyrate : *rac*-lactide; 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): ~10(CH_3 , C-4), 15.80(lactide), 16.66 & 16.75(CH_3 , C-7, 10, 13), 20.51(CH_3 , C-16), ~25(CH_2 , C-3), ~67($\text{CH}(\text{CH}_3)\text{OH}$, C-15), 69.01, 69.19 & 69.43($\text{CH}(\text{CH}_3)\text{O}$, C-6, 9, 12), 72.48(lactide), 72.89($\text{CH}(\text{C}_2\text{H}_5)\text{O}$, C-2) and 169.62 & 169.37($\text{C}=\text{O}$).

2.B7: 2-Hydroxyhexanoate Initiated Polymers.



Gh17-NaHHxAPLA001 (2-hydroxyhexanoic acid : *rac*-lactide; 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 13.93(CH_3 , C-6), 15.82(lactide), 16.66 & 17.16(CH_3 , C-9,12,15), 20.51(CH_3 , C-18), 22.29(CH_2 , C-5), 31.03(CH_2 , C-3), 66.61($\text{CH}(\text{CH}_3)\text{OH}$, C-17), 69.03 & 69.20($\text{CH}(\text{CH}_3)\text{O}$, C-8,11,14), 72.49(lactide) and 169.39, 169.61 & 170.12($\text{C}=\text{O}$).

Gh17-NaHHxAPLA002 (2-hydroxyhexanoic acid : *rac*-lactide; 1 : 12) ^{13}C NMR (CDCl₃, 75 MHz) δ (ppm): 16.66, 17.11(CH₃, C-9,12,15), 20.52(CH₃, C-18), 69.04 & 69.21(CH(CH₃)O, C-8,11,14) and 169.66(C=O).

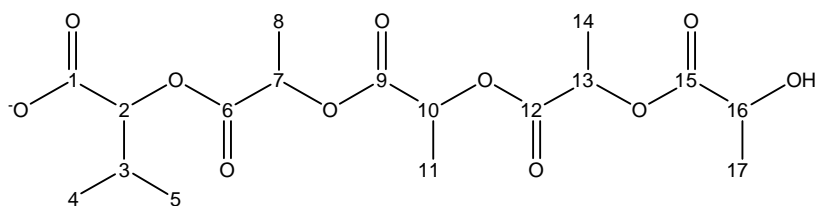
Gh17-KHHxAPLAB002 (2-hydroxyhexanoic acid : *rac*-lactide; 1 : 12) ^{13}C NMR (CDCl₃, 75 MHz) δ (ppm): 13.95(CH₃, C-6) 15.79(lactide), 16.66 & 16.75(CH₃, C-9,12,15), 20.52(CH₃, C-18), 22.33(CH₂, C-5), ~27(C-,4), ~30(CH₂, C-3), ~67 CH(CH₃)OH, C-17), 69.01, 69.19 & 69.43(CH(CH₃)O, C-8,11,14), 72.48(lactide) and 169.37 & 169.62(C=O).

Gh17-NaHHxALPLA001 (2-hydroxyhexanoic acid : L-lactide; 1 : 6) ^{13}C NMR (CDCl₃, 75 MHz) δ (ppm): 13.90(CH₃, C-6), 15.80(lactide), 16.65 & 17.08(CH₃, C-9,12,15), 20.35 & 20.49(CH₃, C-18), 22.25(CH₂, C-5), ~26.5(CH₂, C-4), 30.93(CH₂, C-3), 66.45 & 66.63(CH(CH₃)OH, C-17), 69.03 & 69.49(CH(CH₃)O, C-8,11,14), 72.48(lactide), 169.62, 169.76 & 170.03(C=O) and 175.48(COOH)

Gh17-NaHHxALPLA002 (2-hydroxyhexanoic acid : L-lactide; 1 : 12) ^{13}C NMR (CDCl₃, 75 MHz) δ (ppm): ~13(CH₃, C-6), 15.82(lactide), 16.66, 16.75 & 17.08(CH₃, C-9,12,15), 20.35 & 20.49(CH₃, C-18), 30.95(CH₂, C-3), 66.67(CH(CH₃)OH, C-17), 69.03, 69.49 & 69.61(CH(CH₃)O, C-8,11,14), 72.48(lactide), 169.62(C=O) and ~175(COOH)

Gh17-KHHxALPLAB003 (2-hydroxyhexanoic acid : L-lactide; 1 : 12) ^{13}C NMR (CDCl₃, 75 MHz) δ (ppm): ~13.95(CH₃, C-6), 15.83(lactide), 16.66(CH₃, C-9,12,15), 20.53(CH₃, C-18), 22.6(CH₂, C-5), ~66.7(CH(CH₃)OH, C-17), 69.02 & 69.45(CH(CH₃)O, C-8,11,14) and 169.39 & 169.63.

2.B8: 2-Hydroxyisovalerate Initiated Polymers.



gh17-KHiVAPLA001 (2-hydroxyisovaleric acid : *rac*-lactide; 1 : 6) ^{13}C NMR (CDCl₃, 75 MHz) δ (ppm): 15.80(lactide), 16.66 & 17.15(CH₃, C-8,11,14), 19.27(CH₃, C-4,5), 20.51(CH₃, C-17), ~30(CH, C-3), 66.65(CH(CH₃)OH, C-16), 69.02, 69.19 & 69.44(CH(CH₃)O, C-7,10,13), ~80(CH-O, C-2) and 169.39 & 169.62(C=O).

Gh17-NaHiVAPLA001.1 (2-hydroxyisovaleric acid : *rac*-lactide; 1 : 6) ^{13}C NMR (CDCl₃, 75 MHz) δ (ppm): 15.79(lactide), 16.63, 16.73, 17.08 & 17.40(CH₃, C-8,11,14), 20.06, 20.29 & 20.36(CH₃, C-4,5), 20.48(CH₃, C-17), ~31(CH, C-3), 66.58 & 67.20(CH(CH₃)OH, C-16), 69.02, 69.19, 69.44 & 69.60(CH(CH₃)O, C-7,10,13), 72.04 & 72.48(lactide), 169.37 & 169.61(C=O) and 175.26(COOH).

Gh17-NaHiVAPLA003 (2-hydroxyisovaleric acid : *rac*-lactide; 1 : 6) ^{13}C NMR (CDCl₃, 75 MHz) δ (ppm): 16.67 & 17.08(CH₃, C-8,11,14), 20.51(CH₃, C-17), 66.62(CH(CH₃)OH, C-16), 69.03 & 69.21(CH(CH₃)O, C-7,10,13) and 169.38.

Gh17-NaHiVAPLA004 (2-hydroxyisovaleric acid : *rac*-lactide; 1 : 12) ^{13}C NMR (CDCl₃, 75 MHz) δ (ppm): 15.82(lactide), 16.67, 16.76 & 17.06(CH₃, C-8,11,14), 20.52(CH₃, C-17), ~67(CH(CH₃)OH, C-16), 69.02, 69.20 & 69.45(CH(CH₃)O, C-7,10,13), 72.48(lactide) and 169.38 & 169.63(C=O).

Gh17-NaHiVALPLA001a (2-hydroxyisovaleric acid : L-lactide; 1 : 6) ^{13}C NMR (CDCl₃, 75 MHz) δ (ppm): 15.83(lactide), 16.66 & 17.08(CH₃, C-8,11,14), 20.53(CH₃, C-17), ~67(CH(CH₃)OH, C-16), 69.03 & 69.46(CH(CH₃)O, C-7,10,13) and 169.63(C=O).

Gh17-NaHiVALPLA001b (2-hydroxyisovaleric acid : L-lactide; 1 : 6) ^{13}C NMR (CDCl₃, 75 MHz) δ (ppm): 15.83(lactide), 16.66 & 17.10(CH₃, C-8,11,14), 20.3(CH₃,

C-4,5), 20.51(CH₃, C-17), ~67(CH(CH₃)OH, C-16), 69.04 & 69.53(CH(CH₃)O, C-7,10,13), 72.49(lactide), 169.63 & 170.07(C=O) and 175.45(COOH).

Gh17-NaHiVALPLA002 (2-hydroxyisovaleric acid : L-lactide; 1 : 12) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 15.81(lactide), 16.65 & 17.06(CH₃, C-8,11,14), 20.50(CH₃, C-17), 66.66(CH(CH₃)OH, C-16), 69.02, 69.46 & 69.60(CH(CH₃)O, C-7,10,13), 72.48(lactide) and 169.62(C=O).

Gh17-NaLHiVALPLA001 (2(S)-hydroxyisovaleric acid : L-lactide; 1 : 12) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 16.66 & 17.02(CH₃, C-8,11,14), 20.51(CH₃, C-17), ~67(CH(CH₃)OH, C-16), 69.02 & 69.46(CH(CH₃)O, C-7,10,13), and 169.63(C=O).

Gh17-NaLHiVAPLA001 (2(S)-hydroxyisovaleric acid : *rac*-lactide; 1 : 12) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 15.83(lactide), 16.66, 16.76 & 17.06(CH₃, C-8,11,14), 20.51(CH₃, C-17), 66.62(CH(CH₃)OH, C-16), 69.02 & 69.20(CH(CH₃)O, C-7,10,13), and 169.38 & 169.63(C=O).

Gh17-NaLHiVADPLA001 (2(S)-hydroxyisovaleric acid : D-lactide; 1 : 12) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 15.83(lactide), 16.66, 17.05(CH₃, C-8,11,14), 20.52(CH₃, C-17), ~67(CH(CH₃)OH, C-16), 69.02 & 69.46(CH(CH₃)O, C-7,10,13), and 169.47 & 169.63(C=O).

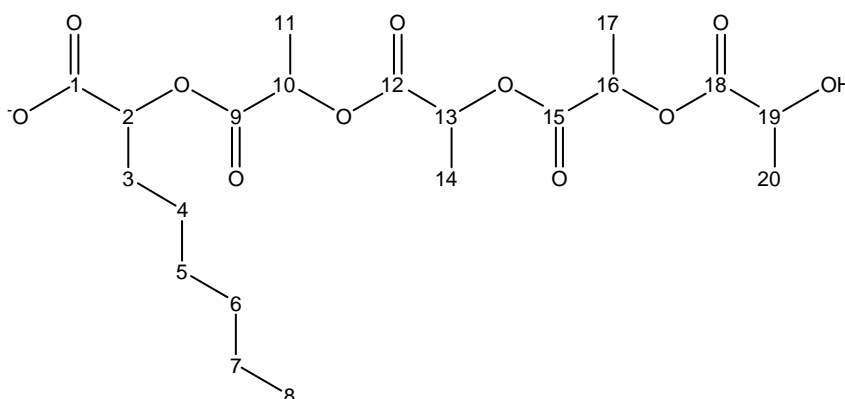
Gh17-NaLHiVALPLA002 (2(S)-hydroxyisovaleric acid : L-lactide; 1 : 12) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 15.83(lactide), 16.66 & 16.98(CH₃, C-8,11,14), 20.51(CH₃, C-17), ~67(CH(CH₃)OH, C-16), 69.02 & 69.46(CH(CH₃)O, C-7,10,13), and 169.63(C=O).

Gh17-NaLHiVA-L+D-PLA001 (2(S)-hydroxyisovaleric acid : L & D-lactide; 1 : 9) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 15.81(lactide), 16.65 & 17.04(CH₃, C-8,11,14), 20.51(CH₃, C-17), ~67(CH(CH₃)OH, C-16), 69.02 & 69.45(CH(CH₃)O, C-7,10,13), 72.48(lactide) and 169.38 & 169.63(C=O).

NaHiVAPLAB001 (2-hydroxyisovaleric acid : *rac*-lactide; 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.80(lactide), 16.66, 16.75 & 17.13(CH_3 , C-8,11,14), 20.53(CH_3 , C-17), ~67($\text{CH}(\text{CH}_3)\text{OH}$, C-16), 69.02, 69.19 & 69.44($\text{CH}(\text{CH}_3)\text{O}$, C-7,10,13), 72.48(lactide) and 169.38 & 169.62($\text{C}=\text{O}$).

NaHiVALPLAB004 (2-hydroxyisovaleric acid : L-lactide; 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.83(lactide), 16.66 & 17.05(CH_3 , C-8,11,14), ~19(CH_3 , C-4,5), 20.51(CH_3 , C-17), 67.60($\text{CH}(\text{CH}_3)\text{OH}$, C-16), 69.03($\text{CH}(\text{CH}_3)\text{O}$, C-7,10,13), 72.48(lactide) and 169.63($\text{C}=\text{O}$).

2.B9: 2-Hydroxyoctanoate Initiated Polymers.



Gh17-KHOctAPLA001 (2-hydroxyoctanoic acid : *rac*-lactide; 1 : 6) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 14.08(CH_3 , C-8), 16.67(CH_3 , C-11,14,17), 20.53(CH_3 , C-20), 22.60(CH_2 , C-7), 31.72(CH_2 , C-3), ~67($\text{CH}(\text{CH}_3)\text{OH}$, C-19), 69.03 & 69.20($\text{CH}(\text{CH}_3)\text{O}$, C-10,13,16) and 169.44($\text{C}=\text{O}$).

Gh17-KHOctAPLA002 (2-hydroxyoctanoic acid : *rac*-lactide; 1 : 12) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 14.07(CH_3 , C-8), 15.83(lactide), 16.67 & 16.76(CH_3 , C-11,14,17), 20.53(CH_3 , C-20), ~67($\text{CH}(\text{CH}_3)\text{OH}$, C-19), 69.02, 69.20 & 69.44($\text{CH}(\text{CH}_3)\text{O}$, C-10,13,16), 72.49(lactide) and 169.38 & 169.63($\text{C}=\text{O}$).

Gh17-KHOctALPLA001 (2-hydroxyoctanoic acid : L-lactide; 1 : 12) ^{13}C NMR (CDCl₃, 75 MHz) δ (ppm): 14.07(CH₃, C-8), 15.84(lactide), 16.66(CH₃, C-11,14,17), 20.53(CH₃, C-20), 22.60(CH₂, C-7), ~67(CH(CH₃)OH, C-19), 69.03 & 69.46(CH(CH₃)O, C-10,13,16) and 169.39 & 169.63(C=O).

Gh17-KHOctALPLA002 (2-hydroxyoctanoic acid : L-lactide; 1 : 6) ^{13}C NMR (CDCl₃, 75 MHz) δ (ppm): 14.08(CH₃, C-8), 16.66(CH₃, C-11,14,17), 20.53(CH₃, C-20), 22.60(CH₂, C-7), 31.70(CH₂, C-3), ~67(CH(CH₃)OH, C-19), 69.03(CH(CH₃)O, C-10,13,16) and 169.63(C=O).

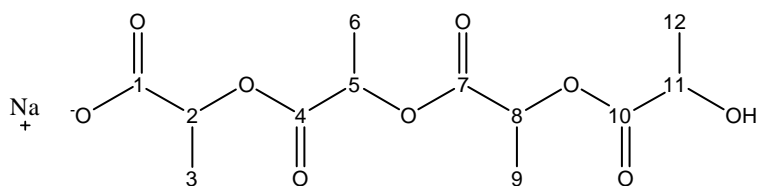
Gh17-KHOctAPLAB010 (2-hydroxyoctanoic acid : *rac*-lactide; 1 : 12) ^{13}C NMR (CDCl₃, 75 MHz) δ (ppm): 14.07(CH₃, C-8), 15.82(lactide), 16.66(CH₃, C-11,14,17), 20.53(CH₃, C-20), 22.59(CH₂, C-7), 28.92(CH₂, C-4,5,6), 31.69(CH₂, C-3), ~67(CH(CH₃)OH, C-19), 69.03 & 69.20(CH(CH₃)O, C-10,13,16) and 169.39 & 169.63(C=O).

Gh17-KHOctALPLAB011 (2-hydroxyoctanoic acid : L-lactide; 1 : 12) ^{13}C NMR (CDCl₃, 75 MHz) δ (ppm): 14.07(CH₃, C-8), 15.83(lactide), 16.66(CH₃, C-11,14,17), 20.53(CH₃, C-20), 22.60(CH₂, C-7), ~28(CH₂, C-4,5,6), ~32(CH₂, C-3), ~67(CH(CH₃)OH, C-19), 69.03 & 69.45(CH(CH₃)O, C-10,13,16) and 169.39 & 169.63(C=O).

Appendix 3: ^{13}C NMR Assignments of Polymer Stereoblocks, Polymer Blends and Stepwise copolymers.

A Poly(lactic acid) stereoblocks.

3.A1 Sodium Lactate Initiated PLA stereoblocks.



Gh17-Na-D-L-PLA001 (Sodium lactate : D-lactide : L-lactide; 1 : 6 : 6) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.83(lactide), 16.66, 17.16 & 17.64(CH_3 , C-3,6,9), 20.52(CH_3 , C-12), ~67($\text{CH}(\text{CH}_3)\text{OH}$, C-11), 69.03 & 69.20($\text{CH}(\text{CH}_3)\text{O}$, C-2,5,8) and 169.38 & 169.64($\text{C}=\text{O}$).

Gh17-Na-L-D,L-PLA001 (Sodium lactate : L-lactide : D,L-lactide; 1 : 6 : 4) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.82(lactide), 16.66, 17.16 & 17.63(CH_3 , C-3,6,9), 20.51(CH_3 , C-12), ~67($\text{CH}(\text{CH}_3)\text{OH}$, C-11), 69.02, 69.20 & 69.45($\text{CH}(\text{CH}_3)\text{O}$, C-2,5,8), 72.48(lactide) and 169.38 & 169.63($\text{C}=\text{O}$).

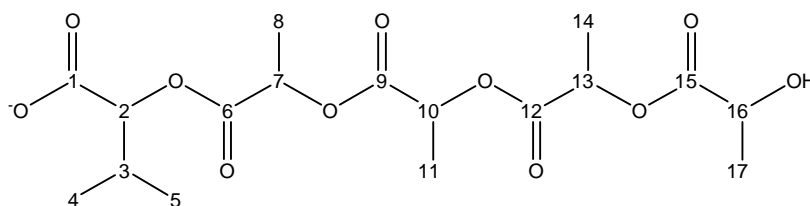
Gh17-Na-D,L-L-PLAS003 (Sodium lactate : *rac*-lactide : L-lactide; 1 : 6 : 6) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.82(lactide), 16.66, 17.10, 17.62 & 17.75(CH_3 , C-3,6,9), 20.52(CH_3 , C-12), ~67($\text{CH}(\text{CH}_3)\text{OH}$, C-11), 69.02 & 69.20($\text{CH}(\text{CH}_3)\text{O}$, C-2,5,8), 72.48(lactide), 72.92(lactoyl lactate) and 169.38 & 169.62($\text{C}=\text{O}$).

Gh17-Na-L-D,L-PLAS004 (Sodium lactate : L-lactide : *rac*-lactide; 1 : 6 : 6) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.82(lactide), 16.66, 16.75 & 17.12(CH_3 , C-3,6,9), 20.52(CH_3 , C-12), ~67($\text{CH}(\text{CH}_3)\text{OH}$, C-11), 69.01, 69.19 & 69.99($\text{CH}(\text{CH}_3)\text{O}$, C-2,5,8), 72.48(lactide) and 169.37 & 169.63($\text{C}=\text{O}$).

Gh17-Na-L-D,L-L-PLAS005 (Sodium lactate : L-lactide : *rac*-lactide : L-lactide; 1 : 4 : 4 : 4) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.82(lactide), 16.66, 17.08 & 17.62(CH_3 , C-3,6,9), 20.51(CH_3 , C-12), ~67($\text{CH}(\text{CH}_3)\text{OH}$, C-11), 69.02, 69.20 & 69.65($\text{CH}(\text{CH}_3)\text{O}$, C-2,5,8), 72.48(lactide) and 169.38 & 169.63($\text{C}=\text{O}$).

Gh17-Na-D,L-D-D,L-PLAS006 (Sodium lactate : *rac*-lactide : D-lactide : *rac*-lactide; 1 : 4 : 4 : 4) ^{13}C NMR (CDCl_3 , 75 MHz) $\delta(\text{ppm})$: 15.83(lactide), 16.66, 17.15 & 17.63(CH_3 , C-3,6,9), 20.51(CH_3 , C-12), 66.63($\text{CH}(\text{CH}_3)\text{OH}$, C-11), 69.03, 69.20 & 69.45($\text{CH}(\text{CH}_3)\text{O}$, C-2,5,8), 72.48(lactide) and 169.38 & 169.62($\text{C}=\text{O}$).

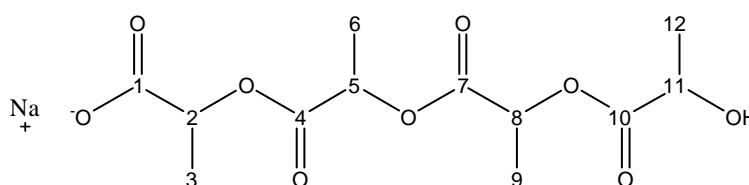
3.A2 Sodium Hydroxyisovalerate initiated stereoblocks.



Gh17-NaLHiVA-L-D-PLA001 (2(S)-hydroxyisovaleric acid : L-lactide : D-lactide; 1 : 6 : 6) ^{13}C NMR (CDCl_3 , 75 MHz) $\delta(\text{ppm})$: 15.39(lactide), 16.65 & 16.99(CH_3 , C-8,11,14), 19.19(CH_3 , C-4,5), 20.50(CH_3 , C-17), 66.63($\text{CH}(\text{CH}_3)\text{OH}$, C-16), 69.01 & 69.45($\text{CH}(\text{CH}_3)\text{O}$, C-7,10,13), and 169.46 & 169.62($\text{C}=\text{O}$).

B Stereocomplex Blends

3.B1 Sodium Lactate Initiated Polymer Blends



gh17-Na-L+D-PLA001 (sodium lactate : L-lactide + sodium lactate : D-lactide; 1 : 9 + 1 : 9) ^{13}C NMR (CDCl_3 , 75 MHz) $\delta(\text{ppm})$:

1) NaLPLA: 15.80(lactide), 16.65, 16.74 & 17.15(CH_3 , C-3,6,9), 20.50(CH_3 , C-12), 66.64($\text{CH}(\text{CH}_3)\text{OH}$, C-11), 69.01 & 69.44($\text{CH}(\text{CH}_3)\text{O}$, C-2,5,8), 72.47(lactide) and 169.62($\text{C}=\text{O}$).

2) NaDPLA: 15.80(lactide), 16.65, 16.75 & 17.24(CH₃, C-3,6,9), 20.50(CH₃, C-12), 66.63(CH(CH₃)OH, C-11), 69.01 & 69.44(CH(CH₃)O, C-2,5,8), 72.47(lactide) and 169.62(C=O).

3) Na-L+D-PLA: 15.29(lactide), 16.66 & 17.24(CH₃, C-3,6,9), 20.52(CH₃, C-12), 66.67(CH(CH₃)OH, C-11), 69.02(CH(CH₃)O, C-2,5,8) and 169.62(C=O).

gh17-Na-L+D-PLA002 (sodium lactate : L-lactide + sodium lactate : D-lactide; 1 : 12 + 1 : 12) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm):

1) NaLPLA: 15.83(lactide), 16.66(CH₃, C-3,6,9), 20.52(CH₃, C-12), ~67(CH(CH₃)OH, C-11), 69.02 & 69.45(CH(CH₃)O, C-2,5,8), 72.48(lactide) and 169.63(C=O).

2) NaDPLA: 15.81(lactide), 16.65 & 17.18(CH₃, C-3,6,9), 20.52(CH₃, C-12), ~67(CH(CH₃)OH, C-11), 69.01 & 69.44(CH(CH₃)O, C-2,5,8), 72.47(lactide) and 169.62(C=O).

3) Na-L+D-PLA: 15.29(lactide), 16.66 & 17.11(CH₃, C-3,6,9), 20.52(CH₃, C-12), ~67(CH(CH₃)OH, C-11), 69.03 & 69.46(CH(CH₃)O, C-2,5,8) and 169.69(C=O).

gh17-Na-L-D+D-L-PLA001 (sodium lactate : L-lactide : lactide + sodium lactate : D-lactide : L-lactide; 1 : 4 : 4 + 1 : 4 : 4) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm):

1) NaLPLA: 15.83(lactide), 16.66(CH₃, C-3,6,9), 20.52(CH₃, C-12), ~67(CH(CH₃)OH, C-11), 69.02 & 69.45(CH(CH₃)O, C-2,5,8), 72.48(lactide) and 169.63(C=O).

2) NaDPLA: 15.81(lactide), 16.65 & 17.18(CH₃, C-3,6,9), 20.52(CH₃, C-12), ~67(CH(CH₃)OH, C-11), 69.01 & 69.44(CH(CH₃)O, C-2,5,8), 72.47(lactide) and 169.62(C=O).

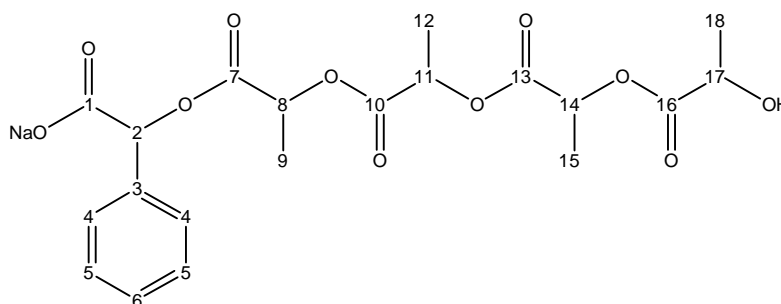
3) Na-L+D-PLA: 15.29(lactide), 16.66 & 17.11(CH₃, C-3,6,9), 20.52(CH₃, C-12), ~67(CH(CH₃)OH, C-11), 69.03 & 69.46(CH(CH₃)O, C-2,5,8) and 169.69(C=O).

Gh17-Na-D,L+D,L-PLAM005 (sodium lactate : *rac*-lactide + sodium lactate : *rac*-lactide; 1 : 10 + 1 : 10) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 15.83(lactide), 16.67, 16.75 & 17.05(CH₃, C-3,6,9), 20.51(CH₃, C-12), ~67(CH(CH₃)OH, C-11), 69.03 & 69.20(CH(CH₃)O, C-2,5,8), 72.49(lactide) and 169.39 & 169.63(C=O).

Gh17-Na-D+L-PLAM006 (sodium lactate : L-lactide + sodium lactate : D-lactide; 1 : 10 + 1 : 10) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.83(lactide), 16.66 & 17.05(CH_3 , C-3,6,9), 20.51(CH_3 , C-12), ~67($\text{CH}(\text{CH}_3)\text{OH}$, C-11), 69.03 & 69.46($\text{CH}(\text{CH}_3)\text{O}$, C-2,5,8), 72.49(lactide) and 169.63($\text{C}=\text{O}$).

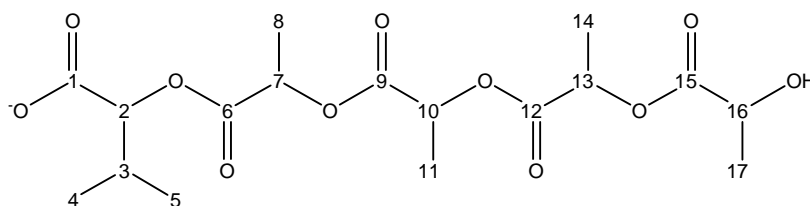
gh17-Na-D,L-D+D,L-L-PLAM007 (sodium lactate : D-lactide : *rac*-lactide + sodium lactate : *rac*-lactide : L-lactide; 1 : 5 : 5 + 1 : 5 : 5) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.81(lactide), 16.65, 16.75, 17.00 & 17.61(CH_3 , C-3,6,9), 20.50(CH_3 , C-12), 66.68($\text{CH}(\text{CH}_3)\text{OH}$, C-11), 69.02, 69.20 & 69.49($\text{CH}(\text{CH}_3)\text{O}$, C-2,5,8), 72.48(lactide) and 169.38 & 169.62($\text{C}=\text{O}$).

3.B2 Sodium Mandelate Initiated Polymer Blends



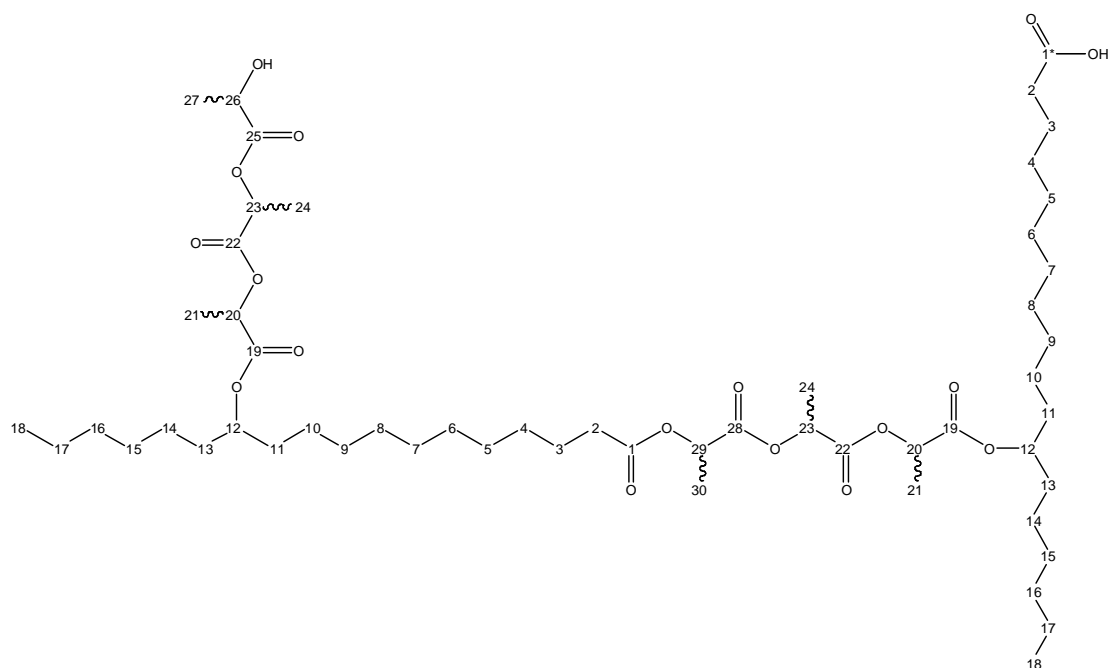
Gh17-NaMan-L+D-PLA001 (sodium mandelate : L-lactide + sodium mandelate : D-lactide; 1 : 9 + 1 : 9) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 16.66(CH_3 , C-9,12,15), 20.50(CH_3 , C-18), 66.7($\text{CH}(\text{CH}_3)\text{OH}$, C-17), 69.03 & 69.46($\text{CH}(\text{CH}_3)\text{O}$, C-8,11,14), 127.7(CH , C-6), 128.33(CH , C-4,5) and 169.63($\text{C}=\text{O}$).

3.B3 Sodium Hydroxyisovalerate Initiated Polymer Blends



gh17-NaLHiV-L+D-PLA001 (Na L-hydroxyisovalerate : L-lactide + Na L-hydroxyisovalerate : D-lactide; 1 : 9 + 1 : 9) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 15.81(lactide), 16.65 & 17.04(CH_3 , C-8,11,14), 20.51(CH_3 , C-17), ~30(CH , C-3), 69.02 & 69.45($\text{CH}(\text{CH}_3)\text{O}$, C-7,10,13), 72.48(lactide), and & 169.63($\text{C}=\text{O}$).

C PLA/12-HSA step-wise copolymers.



Gh17-POLX2 (a) (12-HSA : lactide, 1 : 3 using Sn-oct) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 13.21(CH_3), 14.91(CH_3 , C-18), 15.80, 15.88, 16.06, 19.63(CH_3 , C-21,24,30), 21.69(CH_3 , C-27), 21.77(Toluene), 23.82(CH_2 , C-17), 24.27(CH_2 , C-10,14), 24.73(CH_2 , C-3), 28.24, 28.30, 28.36, 28.54 & 28.83(CH_2 , C-4,5,6,7,8,9,15), 30.83 & 30.99 (CH_2 , C-10* near free hydroxyl on HSA chain), 31.07(CH_2 , C-16), 33.16(CH_2 , C-11,13), 36.51(C-2), 65.86($\text{CH}(\text{CH}_3)\text{OH}$, C-26), 68.17, 68.35, 68.62, & 68.75($\text{CH}(\text{CH}_3)\text{O}$, C-20,23,29), 71.28 & 71.61($\text{CH}-\text{O}$, C-12*), 75.18($\text{CH}-\text{O}$, C-12), 168.34, 168.55, 168.79 & 169.13($\text{C}=\text{O}$, C-19,22,25,28) and 178.69(COOH , 12-HSA).

Gh17-POLX2 (b) (12-HSA : lactide, 1 : 3 using Sn-oct in Toluene [6 hrs]) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 14.47(CH_3 , C-18), 16.22, 17.06, 17.15 & 17.33(CH_3 , C-21,24,30), 20.93(CH_3 , C-27), 21.87(Toluene), 22.95(CH_2 , C-17), 25.07(CH_2 , C-

10,14), 25.55(CH₂, C-3), 29.50 & 29.83(CH₂, C-4,5,6,7,8,9,15), 32.10(CH₂, C-16), 34.22(CH₂, C-11,13), 67.08(CH(CH₃)OH, C-26), 69.42, 69.59 & 69.86(CH(CH₃)O, C-20,23,29), 169.82, 170.04 & 170.37(C=O).

Gh17-POLX2 (c) (12-HSA : lactide, 1 : 3 using Sn-oct in Toluene [12 hrs]) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 14.06(CH₃, C-18), 15.80, 16.66, 16.75 & 16.93(CH₃, C-21,24,30), 20.03 & 20.50(CH₃, C-27), 21.46(Toluene), 22.55(CH₂, C-17), 24.68(CH₂, C-10,14), 25.13(CH₂, C-3), 29.10, 29.20, 29.44 & 29.69(CH₂, C-4,5,6,7,8,9,15), 31.69 & 31.93(CH₂, C-16), 33.94 & 34.03(CH₂, C-11,13), 66.72(CH(CH₃)OH, C-26), 69.03, 69.20 & 69.47(CH(CH₃)O, C-20,23,29), 72.47(CH-OH, C-12*), 76.03(CH-O-, C-12), 169.39, 169.63 & 169.97(C=O), 179.19(COOH).

Gh17-POLX2 (d) (12-HSA : lactide, 1 : 3 using Sn-oct in Toluene [18 hrs]) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 13.93 & 14.06(CH₃, C-18), 15.81, 16.66, 16.75 & 16.93(CH₃, C-21,24,30), 20.04 & 20.51(CH₃, C-27), 21.46(Toluene), 22.55(CH₂, C-17), 24.70(CH₂, C-10,14), 25.14(CH₂, C-3), 29.10, 29.21, 29.45 & 29.70(CH₂, C-4,5,6,7,8,9,15), 31.70, 31.94(CH₂, C-16), 34.03(CH₂, C-11,13), 66.72(CH(CH₃)OH, C-26), 69.02, 69.19 & 69.45(CH(CH₃)O, C-20,23,29), 72.47(CH-OH, C-12*), 76.02 & 76.30(CH-O-, C-12), 169.39, 169.63 & 169.96(C=O).

Gh17-POLX2 (e) (12-HSA : lactide, 1 : 3 using Sn-oct in Toluene [24 hrs]) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 14.47(CH₃, C-18), 16.16, 17.05, 17.14 & 17.98(CH₃, C-21,24,30), 20.49 & 20.90(CH₃, C-27), 21.85(Toluene), 22.95 & 23.03(CH₂, C-17), 25.10(CH₂, C-10,14), 25.53(CH₂, C-3), 29.49, 29.62, 29.85 & 30.09(CH₂, C-4,5,6,7,8,9,15), 31.33, 31.92(CH₂, C-16), 32.09 & 32.33(?), 34.45(CH₂, C-11,13), 67.11(CH(CH₃)OH, C-26), 69.42, 69.59, 69.85 & 69.97(CH(CH₃)O, C-20,23,29), 72.85(CH-OH, C-12*), 76.40 & 76.67(CH-O-, C-12), 169.78, 170.04 & 170.37(C=O).

Gh17-POLX4 (12-HSA : lactide : Na lactate, 2 : 6 : 1) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 14.09(CH₃, C-18), 15.80, 16.64, 16.95 & 17.10(CH₃, C-21,24,30), 20.48 (CH₃, C-27), 22.55, 22.64(CH₂, C-17), 24.76(CH₂, C-10,14), 25.13(CH₂, C-3), 29.01, 29.09, 29.16, 29.37, 29.49 & 29.69(CH₂, C-4,5,6,7,8,9,15), 31.69 & 31.84(CH₂, C-

16), 34.10(CH₂, C-11,13), 37.38(?), 66.67(CH(CH₃)OH, C-26), 69.01, 69.44 & 70.76(CH(CH₃)O, C-20,23,29), 72.10(CH-OH, C-12*), 76.02(CH-O-, C-12), 169.62, 178.68(COOH).

Gh17-POLX5 (a) (12-HSA : lactide : Na lactate (Toluene), 2 : 6 : 1)

¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 14.09(CH₃, C-18), 15.80(lactide), 16.64 & 16.98(CH₃, C-21,24,30), 20.19, 20.32 & 20.46 (CH₃, C-27), 21.45 & 22.62(CH₂, C-17), 24.75(CH₂, C-10,14), 25.12, 25.60 & 26.07(CH₂, C-3), 29.00, 29.15, 29.31, 29.49, 29.62, 29.69 & 29.82(CH₂, C-4,5,6,7,8,9,15), 31.84(CH₂, C-16), 34.10(CH₂, C-11,13), 37.42(?), 66.41, 66.59 & 66.69(CH(CH₃)OH, C-26), 67.73(??) 69.07(CH(CH₃)O, C-20,23,29), 72.11 & 72.47(CH-OH, C-12*), 169.62, 178.68(COOH).

Gh17-SCPLA001 (12-HSA : *rac*-lactide; 1 : 6; Sn-oct, Toluene) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 14.06(CH₃, C-18), 15.83(lactide), 16.66 & 16.94(CH₃, C-21,24,30), 20.53 (CH₃, C-27), 22.55(CH₂, C-17), 24.69(CH₂, C-10,14), 25.14(CH₂, C-3), 29.11, 29.21 & 29.45(CH₂, C-4,5,6,7,8,9,15), 31.71(CH₂, C-16), 33.83 & 34.10(CH₂, C-11,13) & 66.74(CH(CH₃)OH, C-26), 69.04 & 69.50(CH(CH₃)O, C-20,23,29), 76.49(CH-O, C-12) and 169.63.

Gh17-SCPLA002 (12-HSA : *rac*-lactide; 1 : 10; Sn-oct, Toluene) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 11.79, 13.94 & 14.06(CH₃, C-18), 16.67 & 16.76(CH₃, C-21,24,30), 21.47(CH₃, C-27), 22.56(CH₂, C-17), 24.70(CH₂, C-10,14), 25.23(CH₂, C-3), 29.12, 29.27, 29.45 & 29.71(CH₂, C-4,5,6,7,8,9,15), 31.51(CH₂, C-16), 33.97(CH₂, C-11,13), 69.03, 69.20, 69.34 & 69.45(CH(CH₃)O, C-20,23,29), , 76.49(CH-O, C-12) and 169.28 & 169.63(C=O).

Gh17-SCPLA003 (12-HSA : *rac*-lactide; 1 : 10; Sn-oct, Toluene) ¹³C NMR (CDCl₃, 75 MHz) δ(ppm): 13.95 & 14.07(CH₃, C-18), 15.78(lactide), 16.67, 16.94 & 17.60(CH₃, C-21,24,30), 20.53 & 21.47(CH₃, C-27), 22.57 & 22.65(CH₂, C-17), 24.72(CH₂, C-10,14), 25.14(CH₂, C-3), 29.11, 29.23, 29.46 & 29.71(CH₂, C-4,5,6,7,8,9,15), 31.53 & 31.71(CH₂, C-16), 33.97(CH₂, C-11,13), 69.03, 69.20 & 69.46(CH(CH₃)O, C-20,23,29), 72.46(lactide), 72.92(lactoyl lactate), 76.01(CH-O, C-12) and 169.38 & 169.64(C=O).

Gh17-SCPLA004 (12-HSA : *rac*-lactide; 1 : 10; Sn-oct, Toluene) ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 13.95 & 14.07(CH_3 , C-18), 15.80(lactide), 16.67 & 17.61(CH_3 , C-21,24,30), 21.47(CH_3 , C-27), 22.57(CH_2 , C-17), 24.77(CH_2 , C-10,14), 25.17(CH_2 , C-3), 29.11, 29.27, 29.47 & 29.72(CH_2 , C-4,5,6,7,8,9,15), 31.53 & 31.72(CH_2 , C-16), 34.05(CH_2 , C-11,13), 69.03, 69.20 & 69.44($\text{CH}(\text{CH}_3)\text{O}$, C-20,23,29), 72.47(lactide), 72.92(lactoyl lactate), 76.65(CH-O , C-12) and 169.36(C=O).