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ESI

One-pot Two Polymers: ABB' Melt Polycondensation for Linear Polyesters and Hyperbranched Poly(ester-urethane)s Based on Natural L-Amino acids

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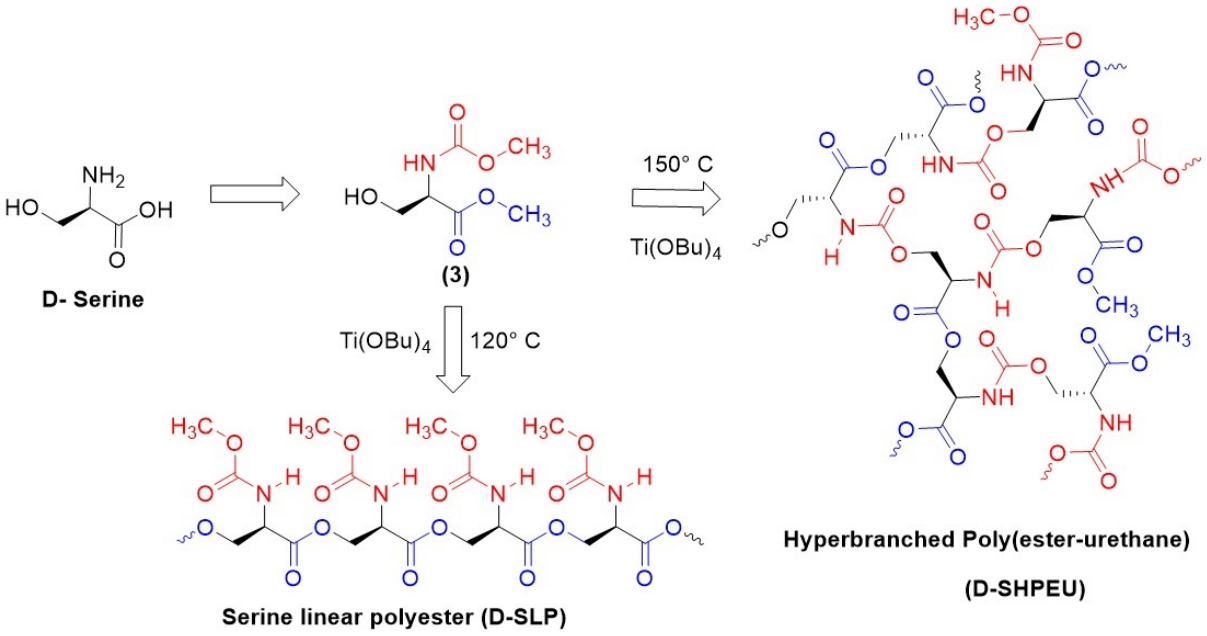


Scheme SS-1: D-serine monomer and polymers

Experimental Section

Synthesis of L-Threonine Linear Polyester (L-TLP): Threonine monomer **(2)** (1.0 g, 5.20 mmoL) and titanium-tetrabutoxide (0.017 g, 0.052 mmoL, 1 mole %) was polymerized at 150 °C for 4 h under nitrogen purge and 2h under vacuum as described for L-SLP. Yield = 0.80 g (96 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 6.22 (s, 1H, -NH), 4.75 (q, 1H, -C**H**-O-CO-), 4.55 (q, 1H, -C**H**-O-CO-NH-), 4.02 (d, 1H, C**H**-CH-O-CO-), 3.96 (d, 1H, C**H**-CH-O-CO-NH-), 3.82 (s, 3H, -NHCOOC**H_3**),3.74 (s, 3H, -COOC**H_3**), 1.57 (d, 3H, C**H_3**-CH-O-CO), 1.34 (d, 3H, C**H_3**-CH-O-CO-NH). ^{13}C-NMR (100 MHZ, $CDCl_3$) δ ppm: 170.73, 159, 60.95, 53.62, 21.64. FT-IR (cm^{-1}): 3573, 3504, 3260, 2975, 2862, 2682, 2361, 1966, 1778, 1644, 1457, 1365, 1285 and 1184.

Synthesis of D-Serine linear poly ester (D-SLP): D-Serine monomer (3) (1.0 g, 5.6 mmoL) and titanium-tetrabutoxide (0.019 g, 0.06 mmoL, 1 mole %) was polymerized at 120 °C for 4 h under nitrogen purge and 2h under vacuum as described for L-SLP. Yield: 0.80 g (98 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 5.92 (s, 1H, -N**H**), 4.64-4.42 (m, 3H,-C**H_2** and -C**H**), 3.81 (s, 3H, -OC**H_3**), 3.72 (s, 3H, -NHCOOC**H_3**). ^{13}C-NMR (100 MHZ, DMSO-d_6) δ ppm: 170.42, 169.92, 168.91, 156.60, 66.0, 63.89, 61.19, 56.65, 52.76, 52.36, 51.82. FT-IR (cm^{-1}): 3313, 2956, 1690, 1528, 1449, 1351, 1248, 1205, 1161 and 1055.

Synthesis of D-Serine Hyperbranched poly(ester-urethane) (D-SHPEU): D-Serine monomer (3) (1 g, 5.6 mmoL)and titanium-tetrabutoxide (0.019g, 0.06 mmoL, 1 mole %) was polymerized at 150 °C for 4 h under nitrogen purge and 2h under vacuum as described for L-SHPEU. Yield: 0.79 g (97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 5.72 (m, 1H, N**H**), 4.66-4.45 (m, 3H, C**H**CH_2OH and CHC**H_2**OH), 3.80 (s, 3H, -OCH_3), 3.72(s, 3H, -$NHCOOCH_3$). ^{13}C-NMR (100 MHZ, DMSO-d_6) δ ppm: 170.51, 170.00, 168.99, 158.63, 156.69, 66.02, 63.96, 61.25, 56.70, 52.87, 52.44, 51.90, 51.73. FT-IR (cm^{-1}): 3317, 2958, 1521, 1449, 1345, 1205 and 1082.

Synthesis of Palmitic ester: Palmitic acid (5.0 g, 19.5 mmoL) was dissolved in MeOH (55 mL) and $SOCl_2$ (2.83 mL, 39 mmoL) was added slowly at ice cold condition and it was refluxed for 12 hours. The solvent was removed and it was poured into brine solution. It was extracted into ethylacetate then Na_2CO_3 solution was added to remove the unreacted acid. The product was purified by passing through silica gel column using 10 % ethylacetate in hexane (9: 1 v/v) as eluent. Yield: 4.8 g (91 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 3.67 (s, 3H, -COO-C**H$_3$**), 2.31 (t, 2H, -CH_2-C**H$_2$**-COO-CH_3),1.61 (m, -C**H$_2$**-CH_2-COO-CH_3), 1.26 (s, 24H, -C**H$_2$**-C**H$_2$**), 0.88 (t, 3H, -CH_2-C**H$_3$**).

Synthesis of n-Octyl urethane; Octyl amine (2g, 15.5 mmoL) was dissolved in 10 wt % Na_2CO_3 (1.97 g, 18.6 mmoL) and methyl chloroformate (1.30 mL, 17 mmoL) in dichloromethane (20 mL) was added. The reaction was continued at 25 °C for 12 h. The solvent was removed and the crude product was purified by passing through silica gel column using 5 % ethyl acetate in hexane (10: 0.5 v/v) as eluent. Yield: 2.8 g (96 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 4.68 (s, 1H, -N**H**), 3.66 (s, 3H, -NHCOOC**H$_3$**), 3.16 (s, 2H, -CH_2-C**H$_2$**-NH-), 1.48 (s, 2H, -CH_2-C**H$_2$**-CH_2-NH-), 1.28 (s, 10H, CH_3-C**H$_2$**-CH_2-), 0.88(s, 3H, -C**H$_3$**).

Model recation-1: Palmitic ester (0.5 g, 2.3 mmol) and cyclohexanol (0.26 g, 2.6 mmol) were taken in a test tube shaped polymerization apparatus. The polycondensation apparatus were made oxygen and moisture free by purging with nitrogen under constant stirring at 90 ^{o}C for about 10 minutes, titanium-tetrabutoxide (0.009g, 0.026 mmol) was added and again degassed for 20 minutes. Then the condensation reaction was carried out at 150 ^{o}C under nitrogen purge for 4h. Yield: 0.65g (90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 4.76 (s, 1H, -CH_2-COO-C_6H_{10}-**H**), 2.31-2.34 (t, 2H, CH_2-C**H$_2$**-COO-C_6H_5), 1.82-1.61 (m, 10H, -C_6**H$_{10}$**), 1.26 (m, 26H, -C**H$_2$**-C**H$_2$**), 0.88 (t, 3H, -CH_2-C**H$_3$**). FT-IR (cm^{-1}): 3499, 2975, 2864, 2682, 2360, 2094, 1966, 1726, 1644, 1457, 1364, 1286, 1183.

Model recation-2: Octyl amine urethane (0.5 g, 2.6 mmol) and cyclohexanol (0.29 g, 2.9 mmol) were taken in a test tube shaped polymerization apparatus. The polycondensation apparatus made oxygen and moisture free by purging with nitrogen under constant stirring at 90 ^{o}C for about 10 minutes, titanium-tetrabutoxide (0.009g, 0.026 mmol) was added and again degassed

for 20 minutes. Then the condensation reaction was carried out at 150 ^{o}C under nitrogen purge for 4h. Yield: 0.3g (30 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 4.68 (s, 1H, -N**H**), 4.33 (s,1H, -NH-COO-C_6H_{10}-**H**), 3.66 (s, 3H, -NHCOOC**H$_3$**), 3.16 (s, 2H, -CH_2-C**H$_2$**-NH-), 1.48 (s, 2H, -CH_2-C**H$_2$**-CH_2-NH-), 1.28 (s, 10H, CH_3-C**H$_2$**-CH_2-), 0.88(s, 3H, -C**H$_3$**). FT-IR (cm^{-1}): 3502, 2977, 2856, 2682, 2361, 2094, 1965, 1724, 1645, 1457, 1364, 1242, 1183.

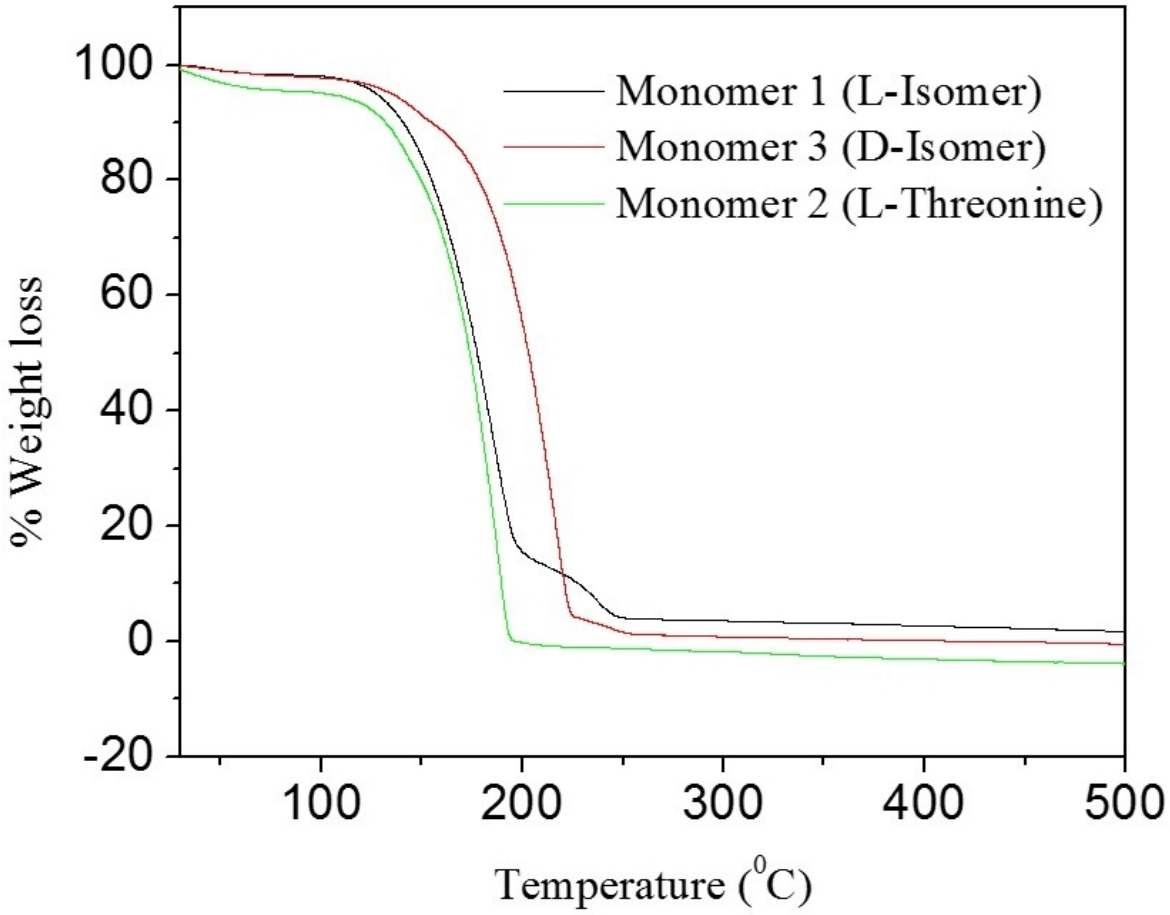


Figure SF-1: Thermalgravimetric analysis of monomers

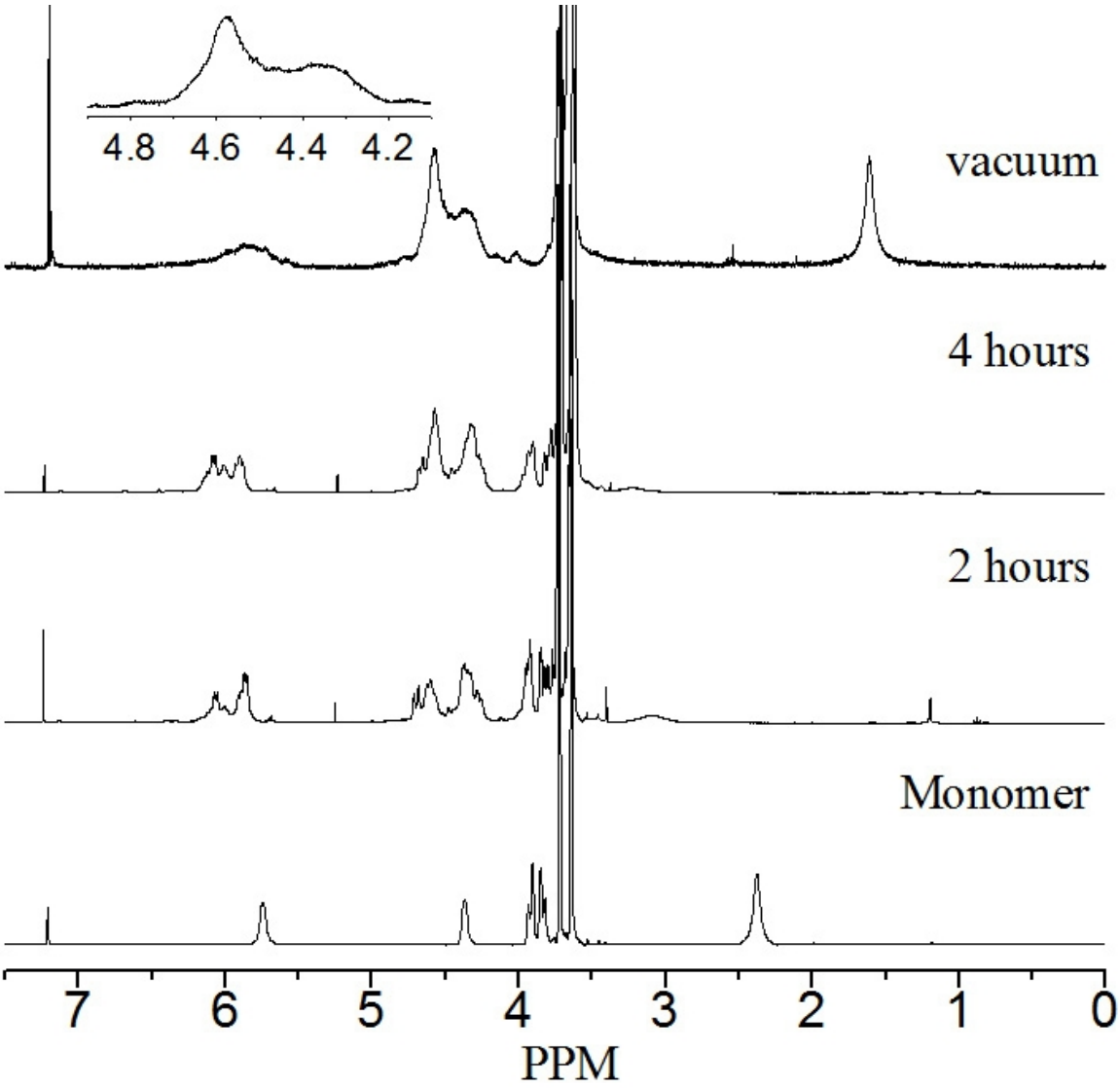


Figure SF-2: ^{1}H- NMR spectra of aliquots of L-SLP

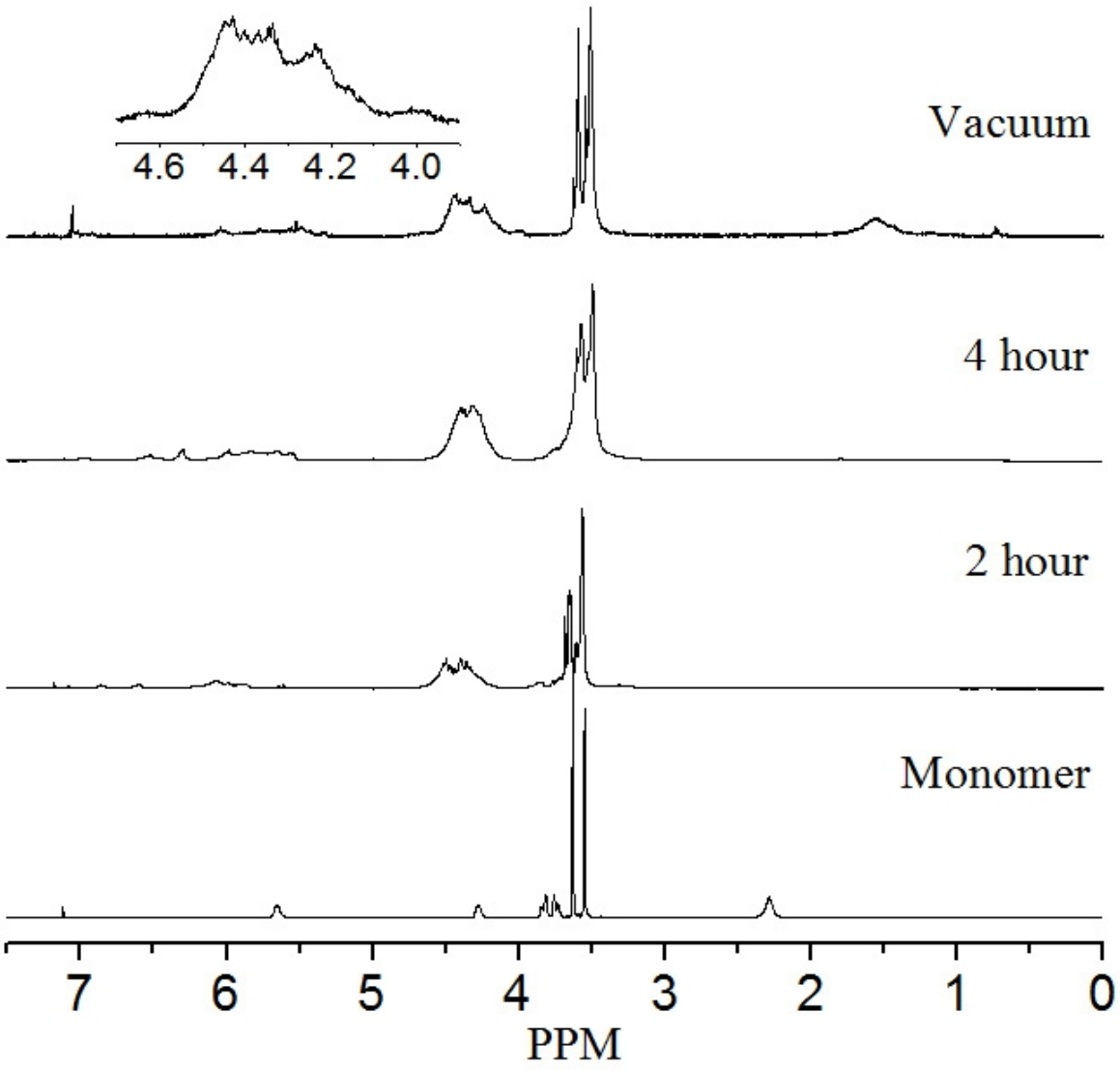


Figure SF-3: ^{1}H- NMR spectra of aliquots of L-SHPEU

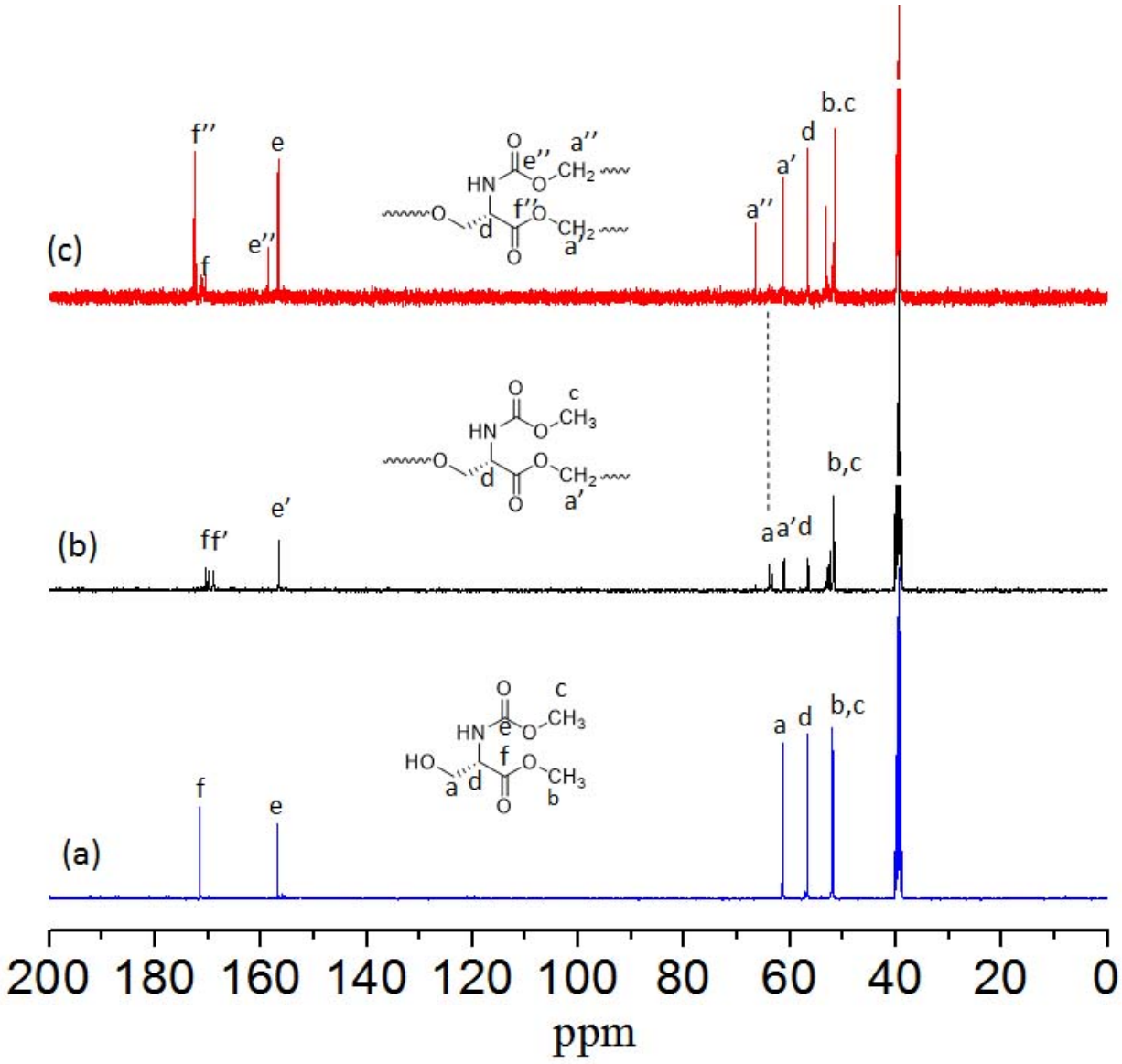


Figure SF-4: ^{13}C NMR of L-serine monomer 1 (a), L-serine linear polyester (L-SLP) (b), and its hyperbranched poly(ester-urethane) (L-SHPEU) (c).

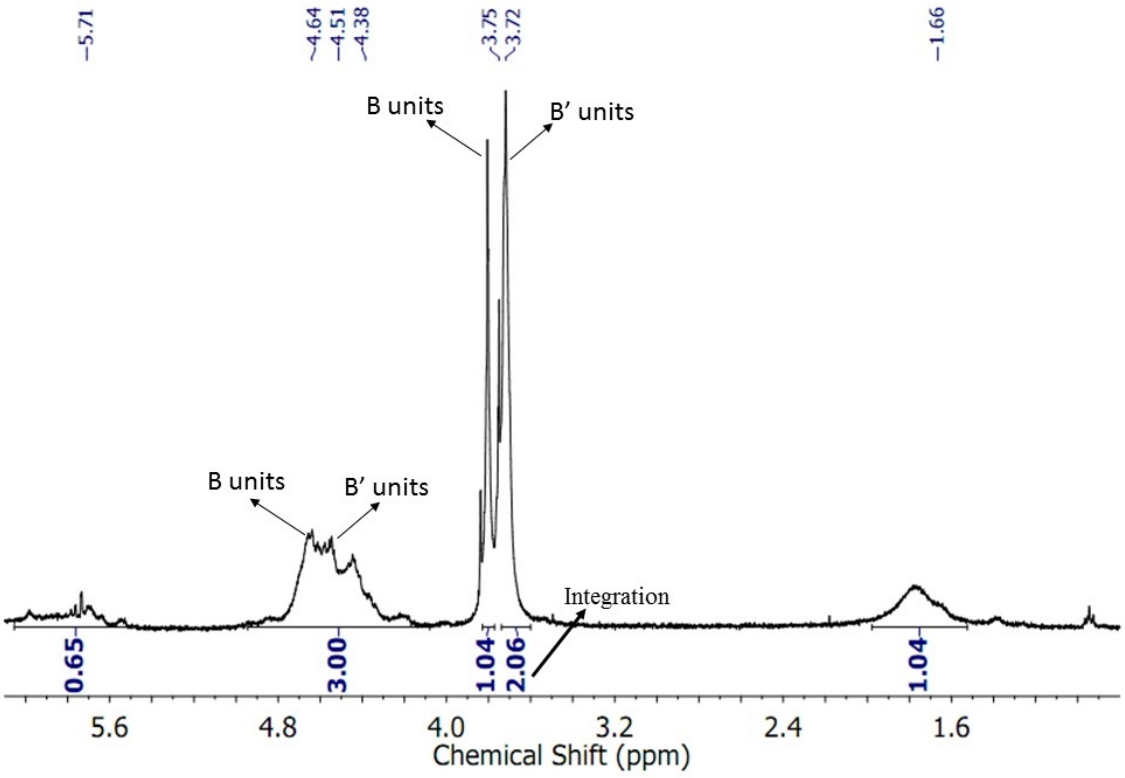


Figure SF-5: Degree of branching calculated from ^{1}H-NMR spectrum of L-SHPEU

Calculation Details:

Degree of Branching (DB) = D+T / D+T+L = 2D /D+T+L

(D= Dendritic; L= Linear and T= terminal)

In the present case,

T+L = B' and D = L = B'-B

Therefore,

DB = 2 (B'-B) / B' + B'-B

Substituting, B' = 2.06 and B = 1.04 (based on NMR in SF-5),

DB = 2/3 = 66 %

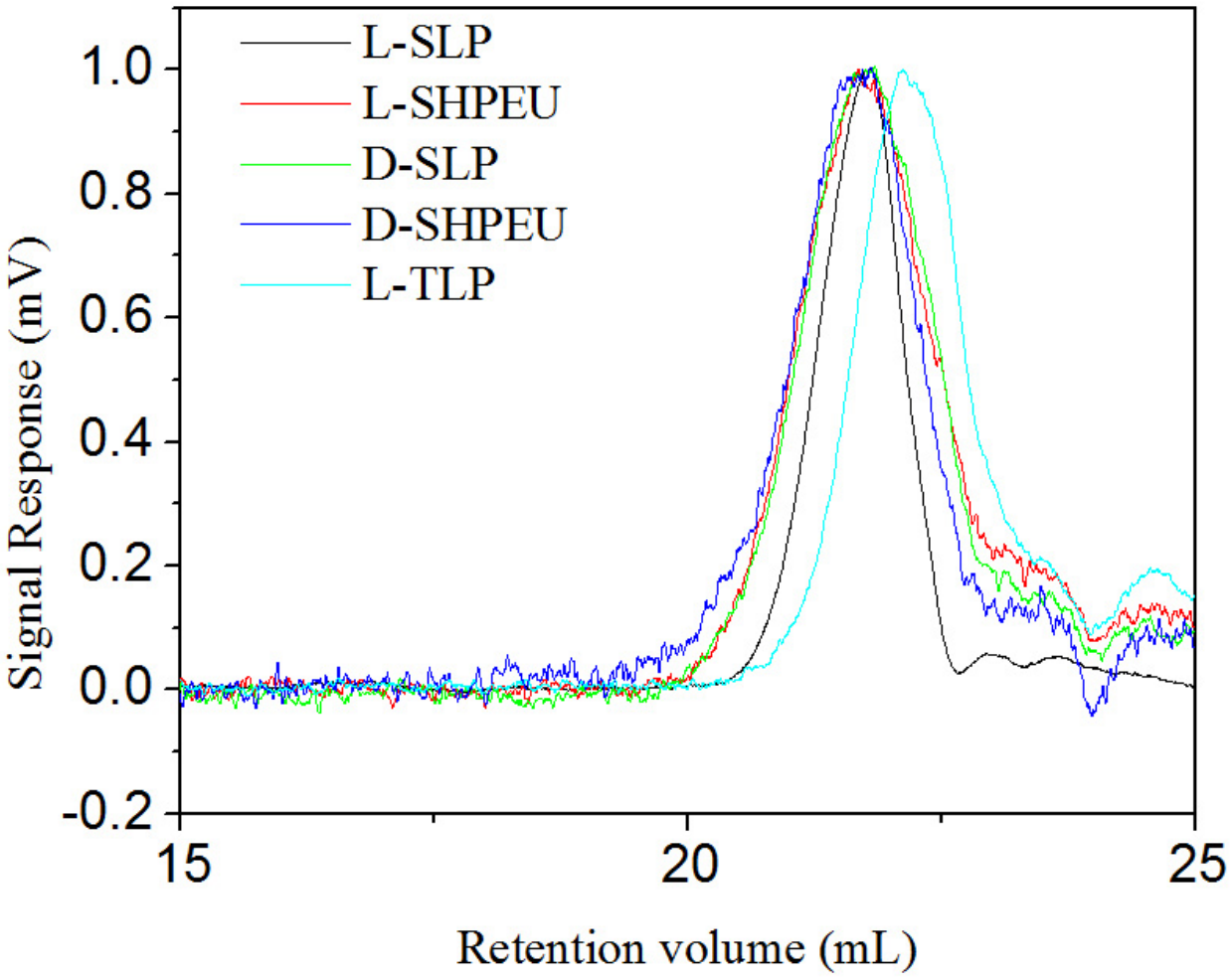


Figure SF-6: GPC plots of polymers

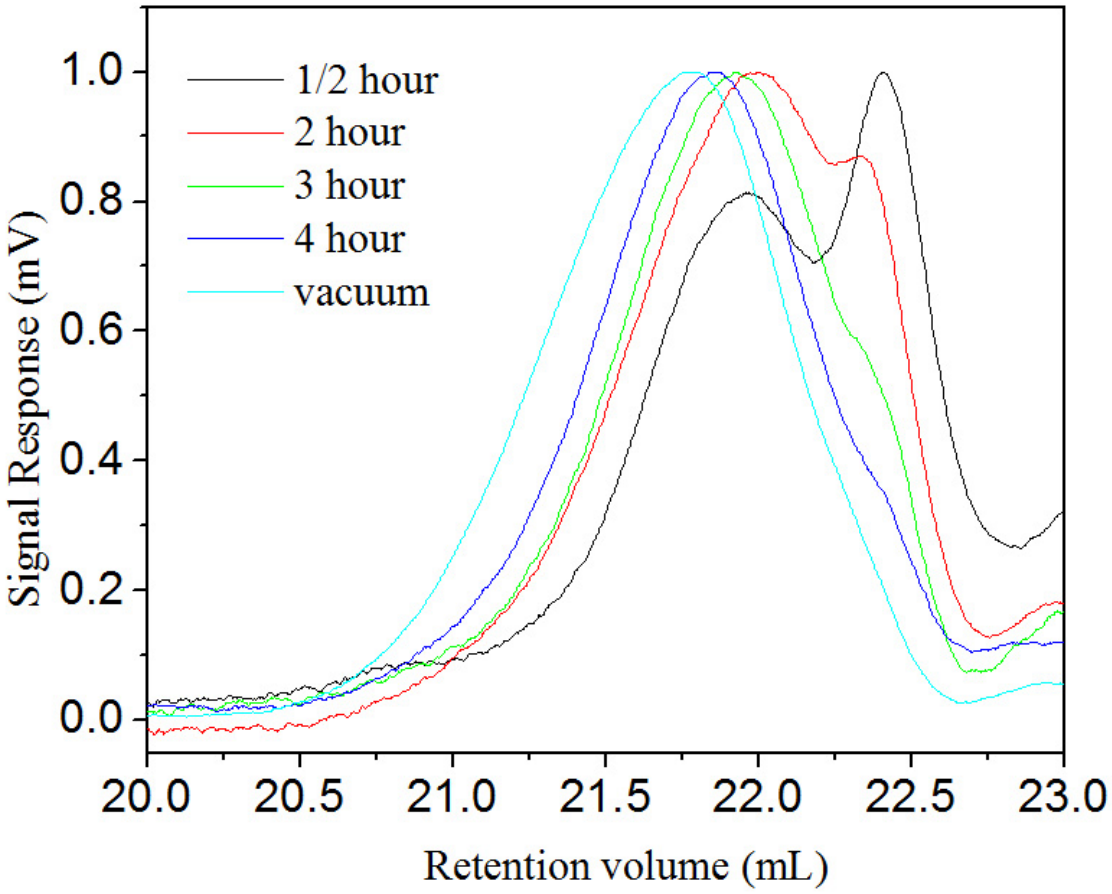


Figure SF-7: GPC Plots of aliquots of L-SLP

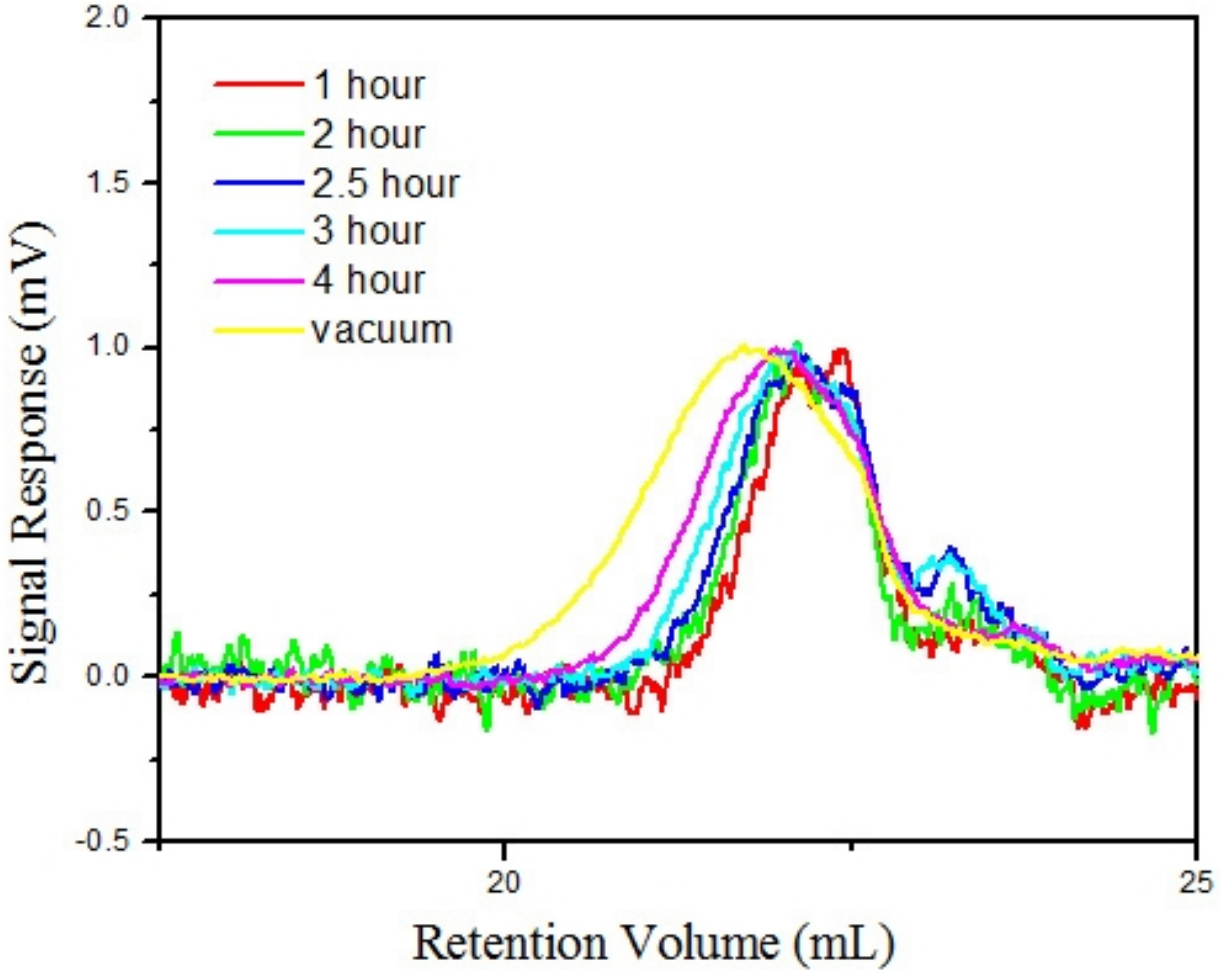


Figure SF-8 : GPC plots of aliquots of L-SHPEU

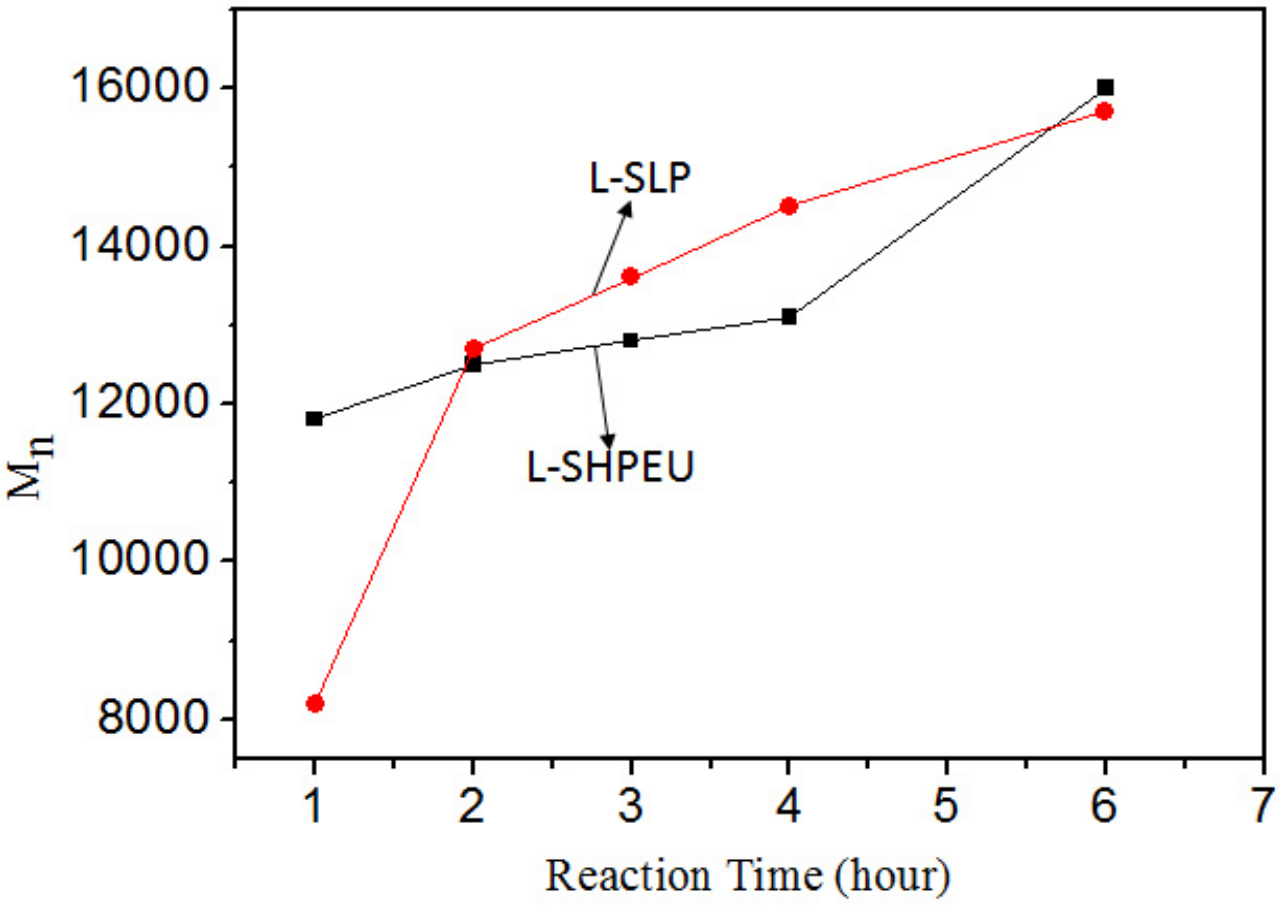


Figure SF-9: Plots of polymerization time vs molecular weights at 120 °C and 150 °C.

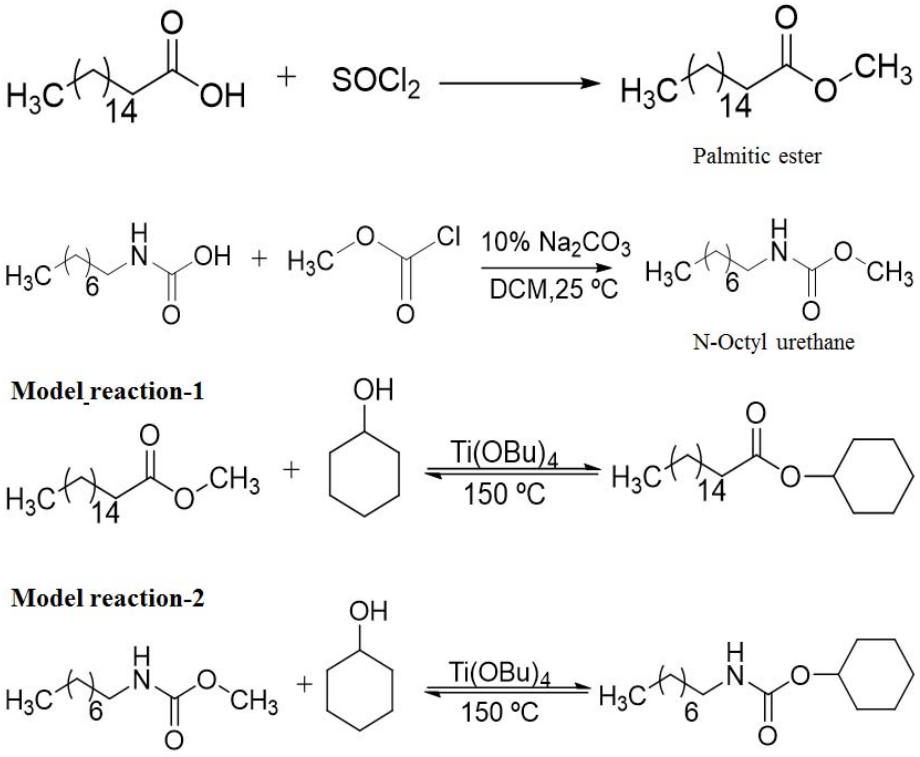
Table ST- 1. *Molecular weights and thermal properties of linear and hyperbranched polymers*

Polymer	Monomer	Polymerization Temperature (°C)	M_n[a] (g/mol)	M_wa (g/ml)	T_g[b] (°C)	T_D[c] (°C)
L-SLP	1a	120	15700	18300	4.3	185
D-SLP	3a	120	11700	20100	5.9	208
L-SHPEU	1a	150	16600	20100	55.0	211
D-SHPEU	3a	150	18300	24300	40.0	215
L-TLP	2a	150	8400	13300	-27.8	167

a) Molecular weights are determined by GPC in dimethyl formamide at 25 °C using polystyrene standards. b) Determined by DSC under nitrogen atmosphere at 10°/min heating rate. c) Determined by TGA under nitrogen atmosphere.(T_D decomposition starting temperature)

Table ST-2. GPC molecular weights of HB Polymer aliquots at different time intervals.

Time	M_n	M_w	PDI
1 Hour	10,800	11600	1.07
2 Hour	11,800	13,300	1.12
2.5 Hour	12,100	14,200	1.17
3 Hour	12,700	14,500	1.14
4 Hour	13,100	15,300	1.17
6 Hour (vacuum)	16,000	22,700	1.4



Scheme SS-2: Synthesis of model compounds

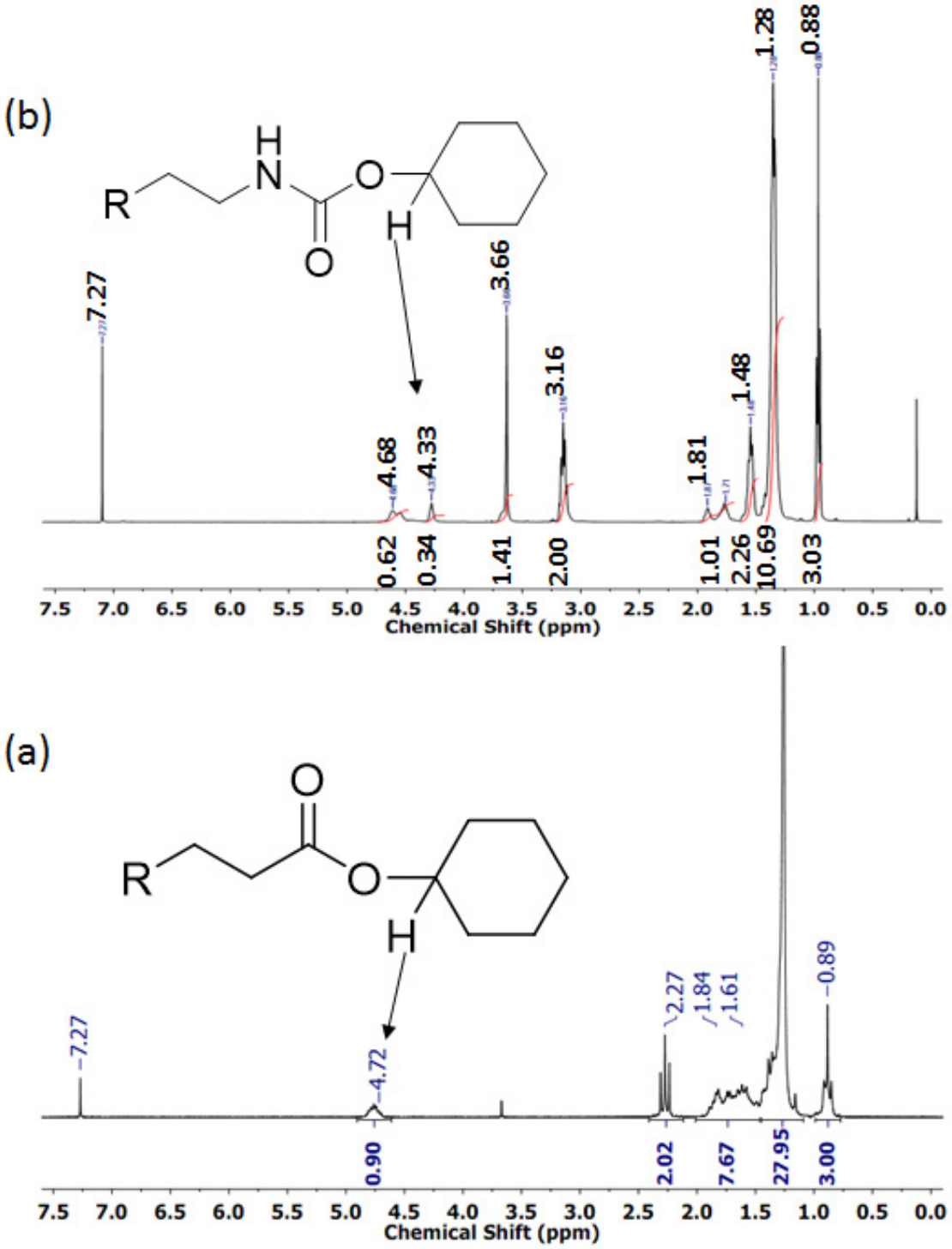


Figure SF-10: NMR spectra of ester (a) urethane (b) model compounds

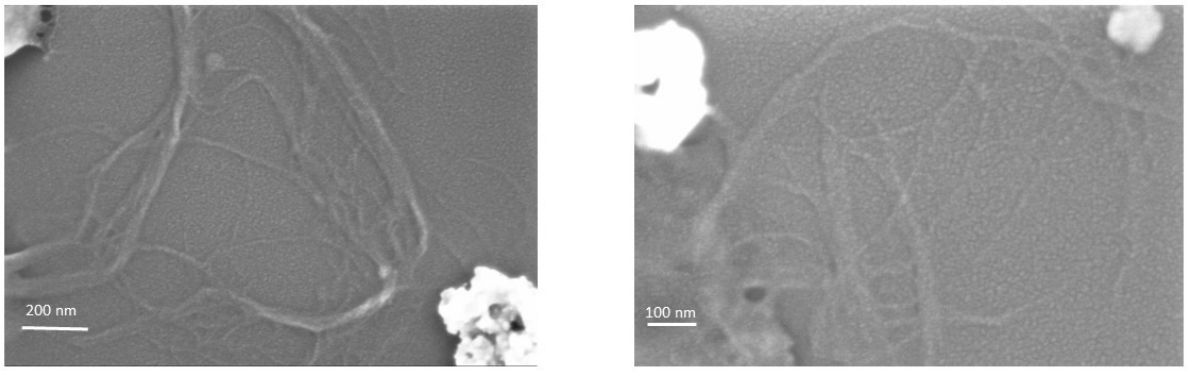


Figure SF-11: FE-SEM images of L-SLP

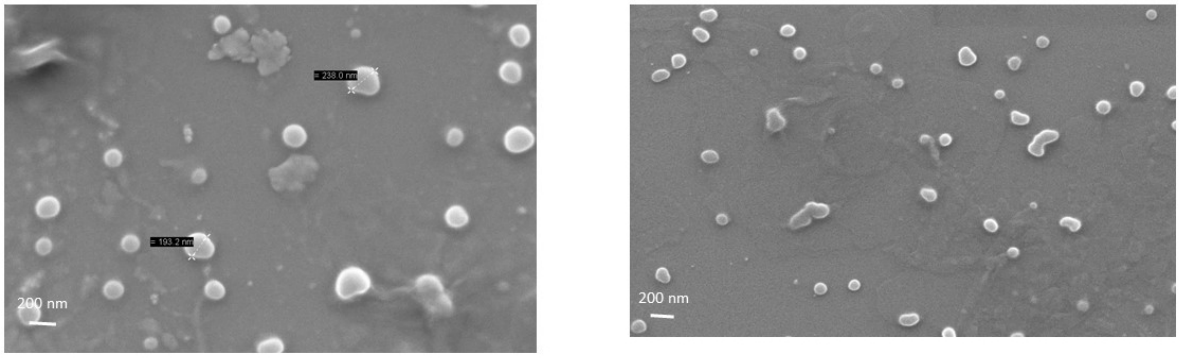


Figure SF-12: FE-SEM images of L-SHPEU

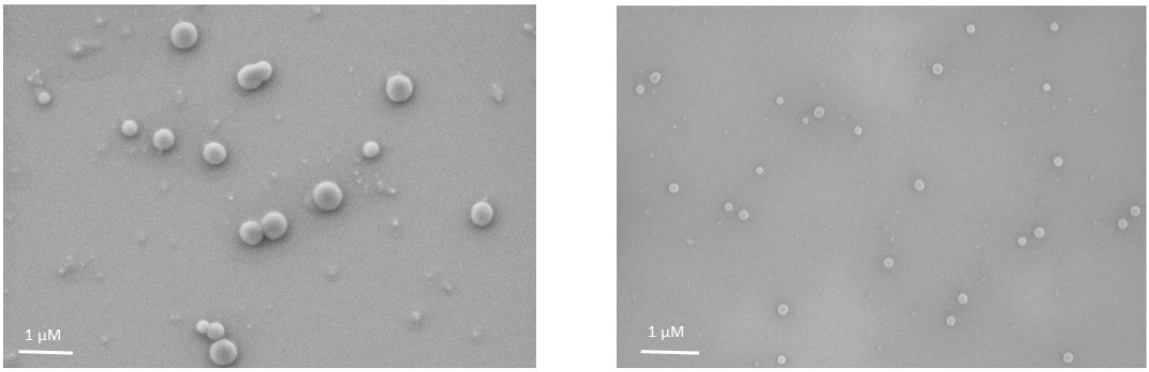


Figure SF-13: FE-SEM images of L-TLP

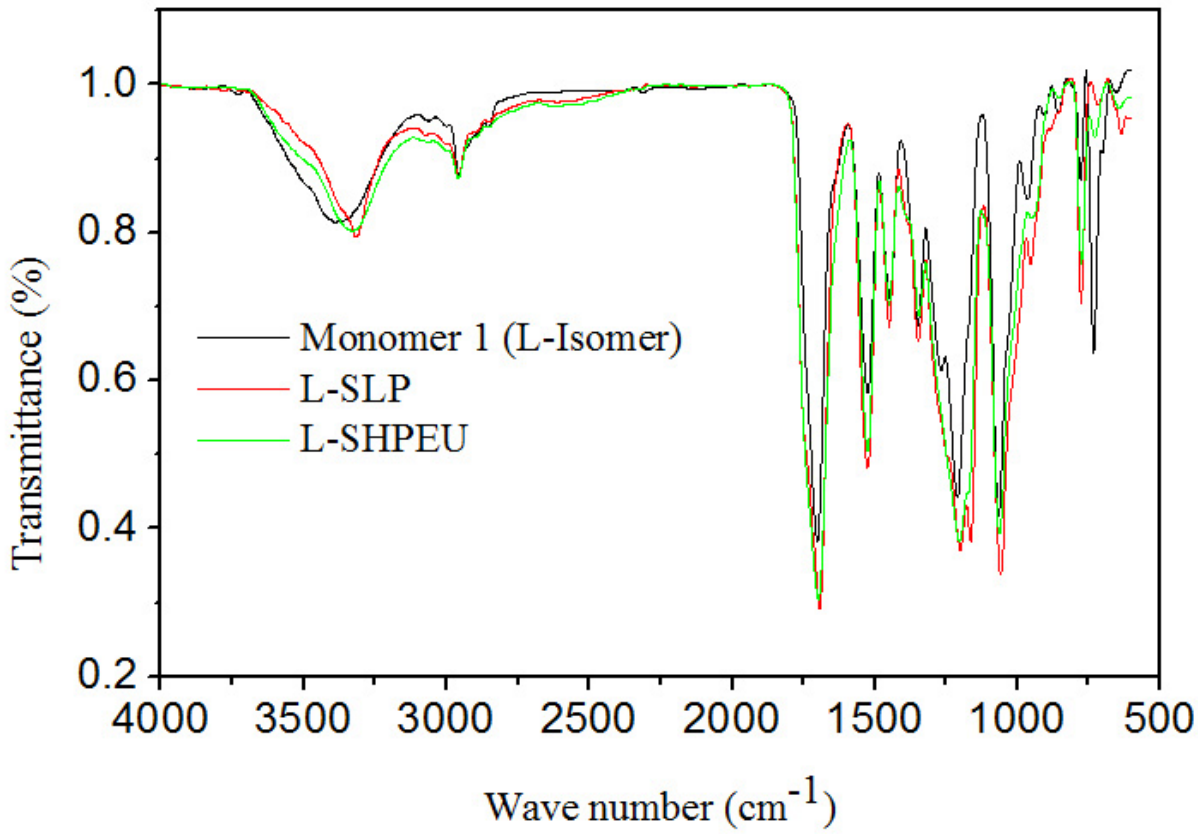


Figure SF-14: FT-IR spectra of polymers

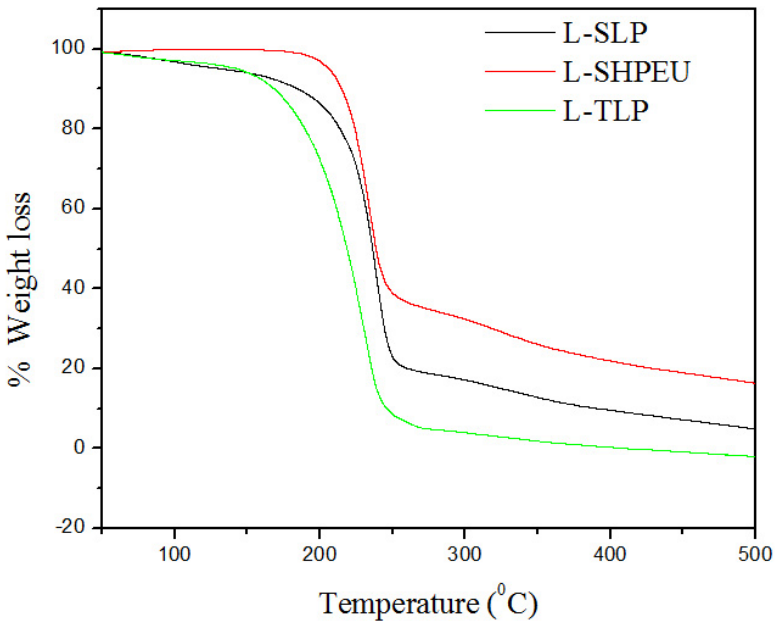


Figure SF-15: TGA plots of aliquots of L-SLP, L-SHPEU and L-TLP.

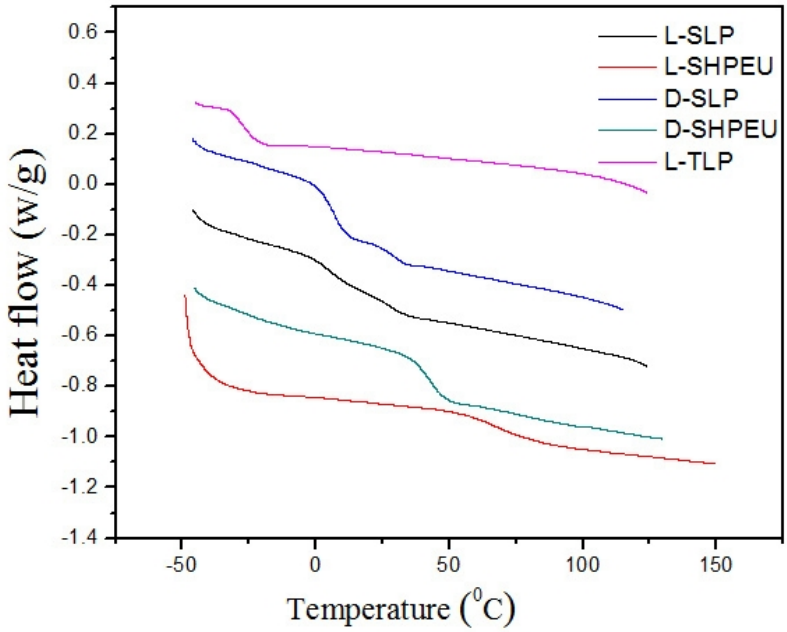


Figure SF-16: DSC Thermograms of polymers

Note: TGA analysis of these polymers revealed that all these polymers were thermally stable up to 220 °C. DSC analysis of the polymers exhibited only glass transition temperatures in the range of -27 °C to 5 °C with respect to their structure.

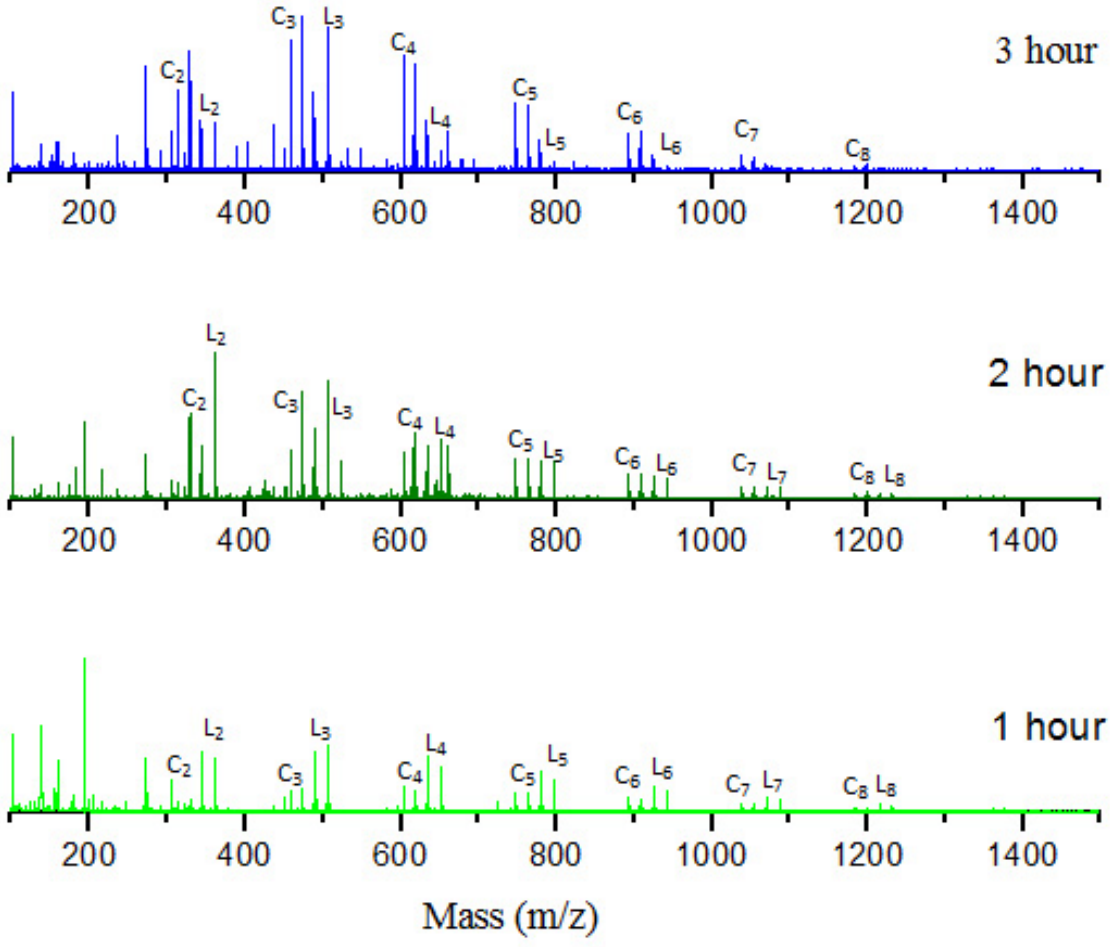


Figure SF-17. MALDI-TOF spectra for HB aliquots collected at 1h, 2h and 3 h.

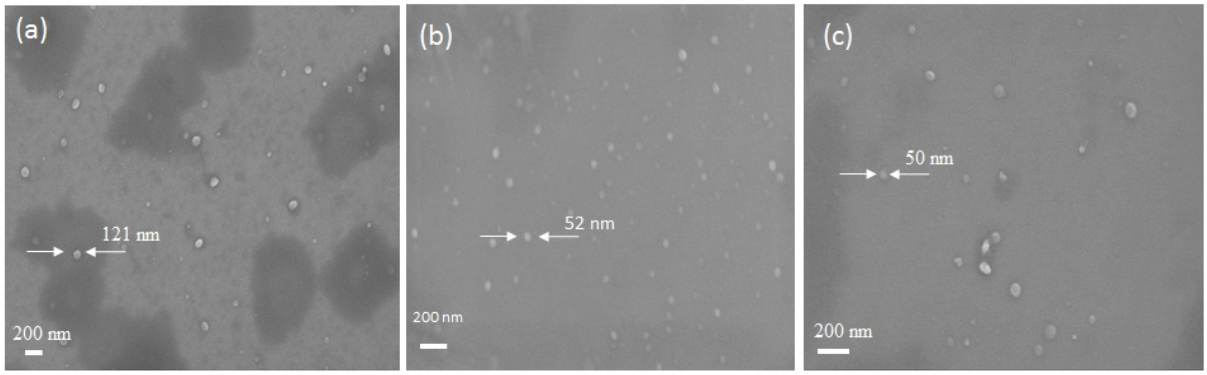


Figure SF-18. FE-SEM images of HB Aliquots Mn = 11,000 (a), Mn =12,700 (b), Mn = 13,100 (c)