SUPPORTING INFORMATION

Eight-armed Polydiacetylene under Benzoxazine Dimer Branched Polylactide: A Structural Combination for Reversible Thermochromic Effect and Its Model Case for Free-Standing Poly(lactic acid) Film

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Synthesis of linear polylactide conjugated diacetylene (linear PLLA-DA)

Phenol (37.8 mg, 0.4 mmol), tin(II) 2-ethylhexanoate (40.5 mg, 0.1 mmol), and L-lactide (1441.4 mg, 10 mmol) were dried under vacuum for 3 hours. The ring opening polymerization was performed under N_2 at 120 ˚C in bulk state until it becomes a viscous. The product was precipitated in cold diethyl ether to obtain linear polylactide with 98 %conversion. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 7.36 (m, 2H, Ar-H), 7.07 (m, 1H, Ar-H), 6.90 (t, 1H, Ar-H), 6.80 (d, J = 8.37 Hz, 1H, Ar-H), 5.14 (dd, J = 6.89, 13.97 Hz, 39H, -OCH(CH3)C(O)- of PLLA), 4.33 (d, J = 6.88 Hz, 1H, terminal -OC(O)CH(CH3)-OH), 1.55 (t, 120H, OCH(CH3)C(O)- of PLLA). ^{1}H NMR analysis indicated a DP_n of 20 lactide units per chain. GPC analysis indicated M_n = 2999 g mol^{-1} and M_w/ M_n = 1.10.

The conjugation reaction of linear polylactide with 10,12-pentacosadiynoic acid (149.8 mg, 0.4 mmol) was proceeded as the same procedure as 4BzD-8PLLA-8DA to obtain PLLA-DA with 92 %yield. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 7.36 (d, J = 8.35 Hz, 2H, Ar-H), 7.06 (d, J = 7.50 Hz, 1H, Ar-H), 6.89 (m, 1H, Ar-H), 6.79 (d, J = 8.33 Hz, 1H, Ar-H), 5.14 (dd, J = 6.92, 14.01 Hz, 36H, -OCH(CH3)C(O)- of PLLA), 4.34 (s, 1H, terminal -OC(O)CH(CH3)-OH), 2.51 (s, 2H, -OC(O)CH2- of DA), 2.22 (t, 4H, -(CH2)C≡C- of DA), 1.55 (t, 111H, OCH(CH3)C(O)- of PLLA), 1.25 (m, 32H, -CH2- of DA) 0.86 (t, 3H, -CH3 of DA). GPC analysis indicated M_n = 3099 g g mol^{-1} and M_w/ M_n = 1.00.

Synthesis of 4 arms polylactide conjugated diacetylene (4PLLA-4DA)

Pentaerythritol (27.2 mg, 0.2 mmol) was used as initiator for ring opening polymerization of L-lactide (2882.8 mg, 20 mmol) in bulk at 120 °C with tin(II) 2-ethylhexanoate catalyst (81.0 mg, 0.2 mmol). At the end of the reaction, the medium was viscous. The product obtained was precipitated in cold diethyl ether and dried under vacuum to obtain 4 arms polylactide (4PLLA) with the yield of 95%. ^{1}H NMR (500 MHz, $CDCl_3$, ppm):

5.14 (d, J = 7.11 Hz, 44H, -OCH(CH3)C(O)- of PLLA), 4.34 (s, 1H, terminal -OC(O)CH(CH3)-OH), 3.51 (m, 2H, C(CH2)-O-PLLA), 1.56 (t, 135H, OCH(CH3)C(O)- of PLLA). ^{1}H NMR analysis indicated a DP_n of 22 lactide units per chain. GPC analysis indicated M_n = 19963 g mol^{-1} and M_w/ M_n = 1.21.

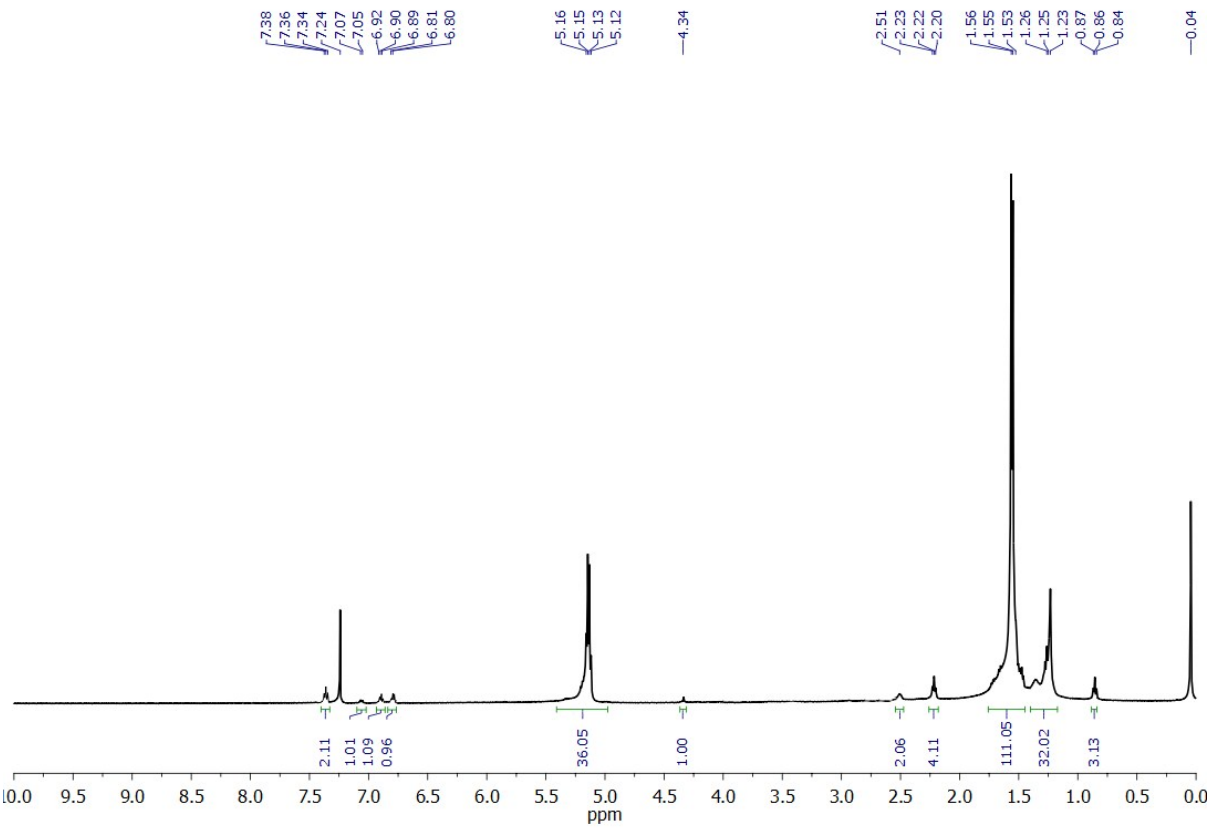
4PLLA and 10,12-pentacosadiynoic acid (149.8 mg, 0.4 mmol) was conjugated as the same procedure as 4BzD-8PLLA-8DA to obtain 4PLLA-4DA with 87 %yield. ^{1}H NMR (500 MHz, $CDCl_3$, ppm):), 5.14 (dd, J = 6.89, 13.89 Hz, 32H, -OCH(CH3)C(O)- of PLLA), 4.35 (s, 1H, terminal -OC(O)CH(CH3)-OH), 3.49 (m, 2H, C(CH2)-O-PLLA), 2.58 (s, 2H, -OC(O)CH2- of DA), 2.22 (s, 4H, -(CH2)C≡C- of DA), 1.48 (t, 131H, OCH(CH3)C(O)- of PLLA and -CH2- of DA) 0.86 (t, 3H, -CH3 of DA).

Synthesis of hyperbranched polylactide conjugated diacetylene (mPEI-PLLA-DA)

Ring opening polymerization of L-lactide (4571.7 mg, 31.7 mmol) was proceeded in bulk at 120 °C with tin(II) 2-ethylhexanoate catalyst (81.0 mg, 0.2 mmol) by using branched polyethyleneimine (93.5 mg, 1.6 mmol) as an initiator. The crude product was precipitate in cold methanol to obtain hyperbranched polylactide (mPEI-PLLA) at 98 %yield. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 5.14 (dd, J = 6.81, 13.89 Hz, 1634H, -OCH(CH3)C(O)- of PLLA), 4.34 (s, 43H, terminal -OC(O)CH(CH3)-OH), 3.72 (dd, J = 8.65, 14.35 Hz, 172H, -NH- and –NH2 of mPEI), 1.54 (m, 5031H, OCH(CH3)C(O)- of PLLA). ^{1}H NMR spectrum suggested 43 polylactide chains with DP_n of 19 lactide units per chain on PEI molecule.

10,12-pentacosadiynoic acid (50.0 mg, 0.13 mmol) was conjugated with -OH group of polylactide as the same procedure as 4BzD-8PLLA-8DA to obtain mPEI-PLLA-DA. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 5.14 (dd, J = 6.85, 13.89 Hz, 903H, -OCH(CH3)C(O)- of PLLA), 4.34 (s, 43H, terminal -OC(O)CH(CH3)-OH), 3.59 (d, J = 126.48 Hz, 172H, mPEI), 2.58 (t,

86H, -OC(O)CH2- of DA), 2.22 (t, 172H, -(CH2)C≡C- of DA), 1.54 (m, 4214H, OCH(CH3)C(O)- of PLLA and -CH2- of DA), 0.86 (t, 129H, -CH3 of DA).



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87 **Figure S1.** ^{1}H NMR of PLLA-DA**.**

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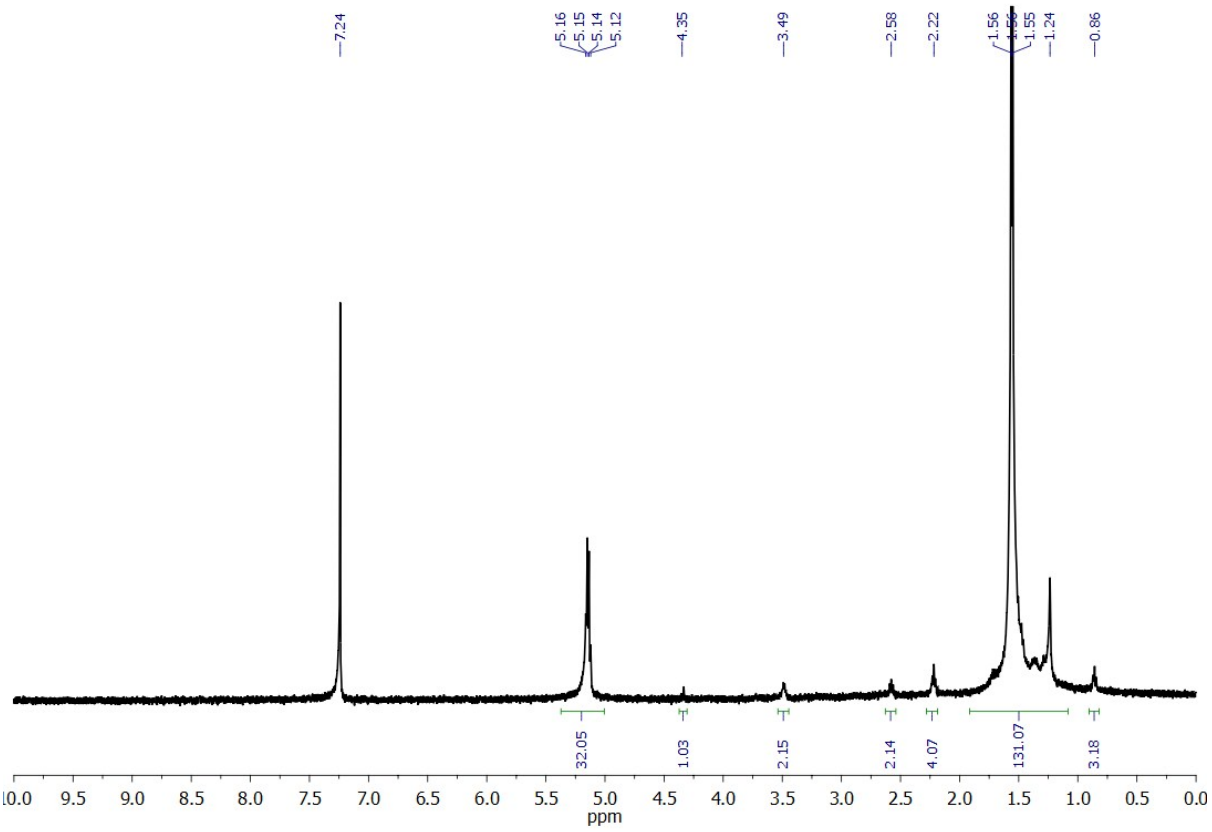

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90 **Figure S2.** ^{1}H NMR of 4PLLA-4DA**.**

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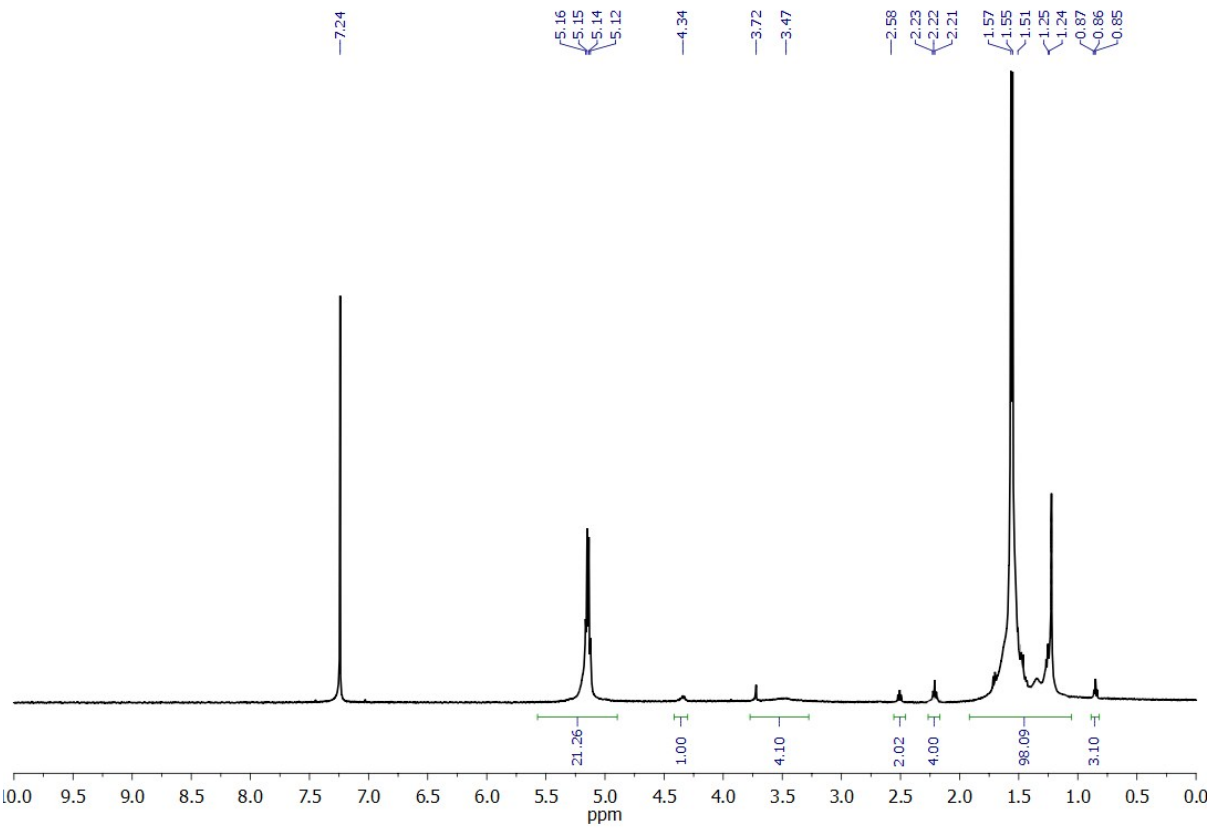

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93 **Figure S3.** ^{1}H NMR of mPEI-PLLA-DA.

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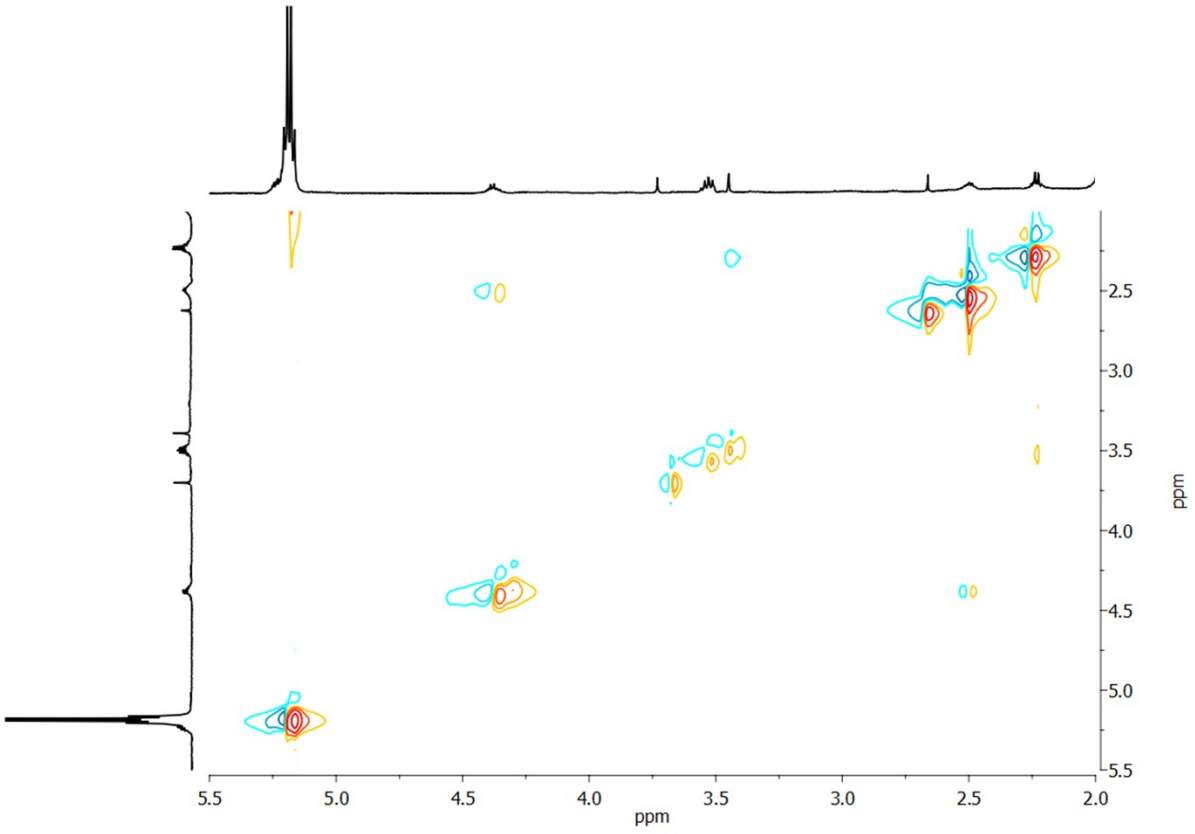

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96 **Figure S4.** TOCSY NMR of 4BzD-8PLLA-8DA.

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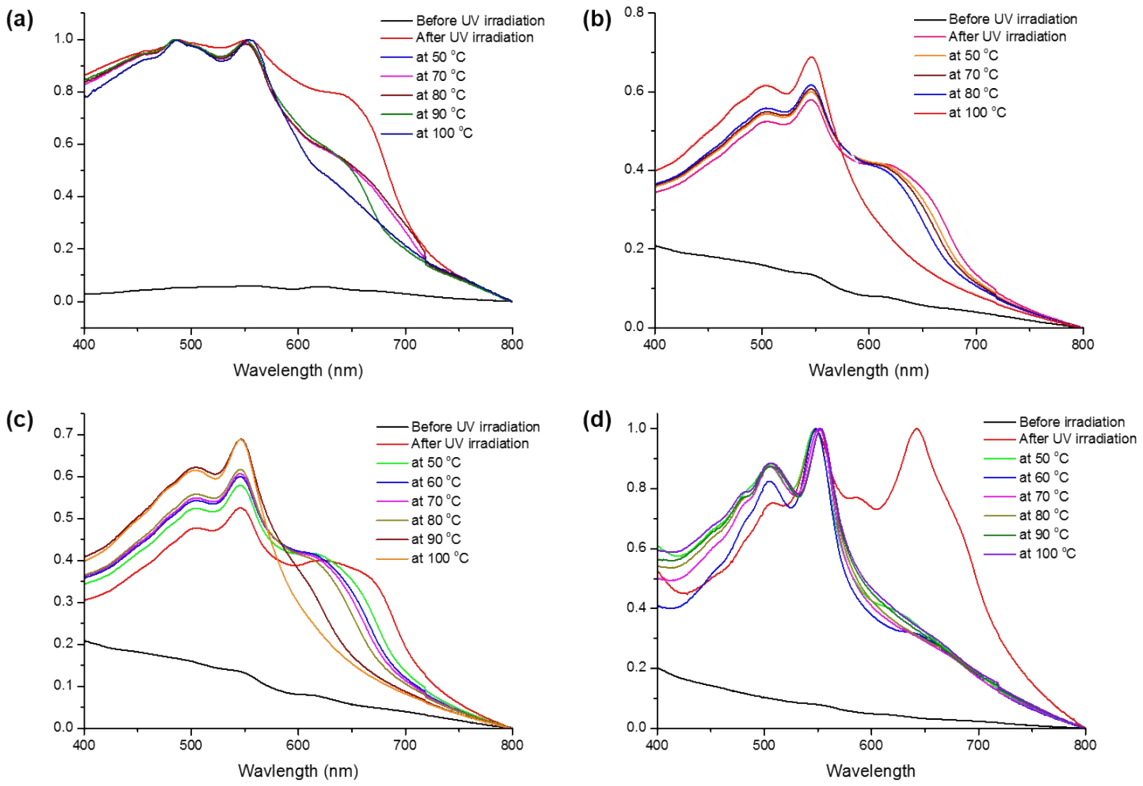

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99 **Figure S5**. UV-Vis spectra of (a) DA, (b) PLLA-DA, (c) 4PLLA-4DA, and (d) mPEI-PLLA-

100 DA.

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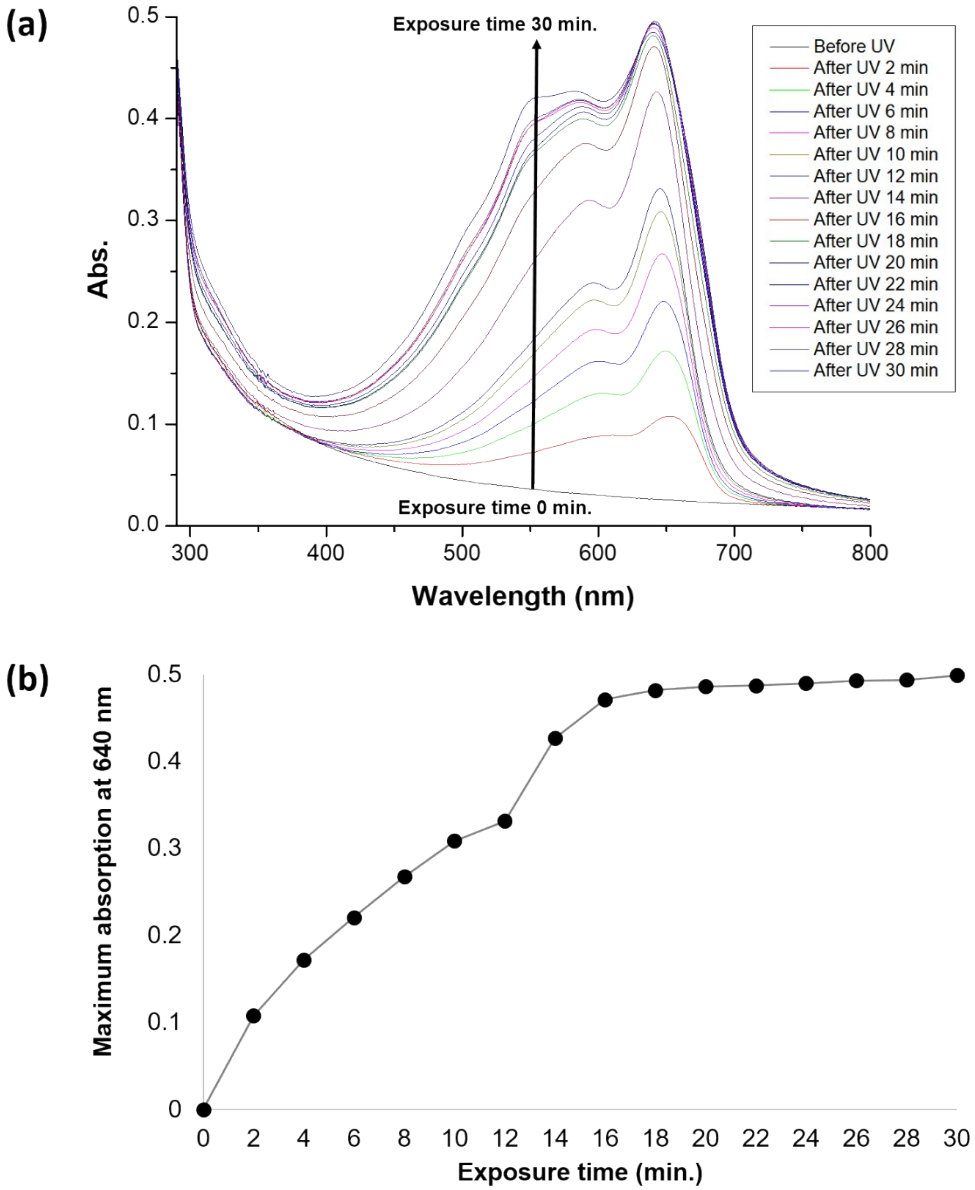

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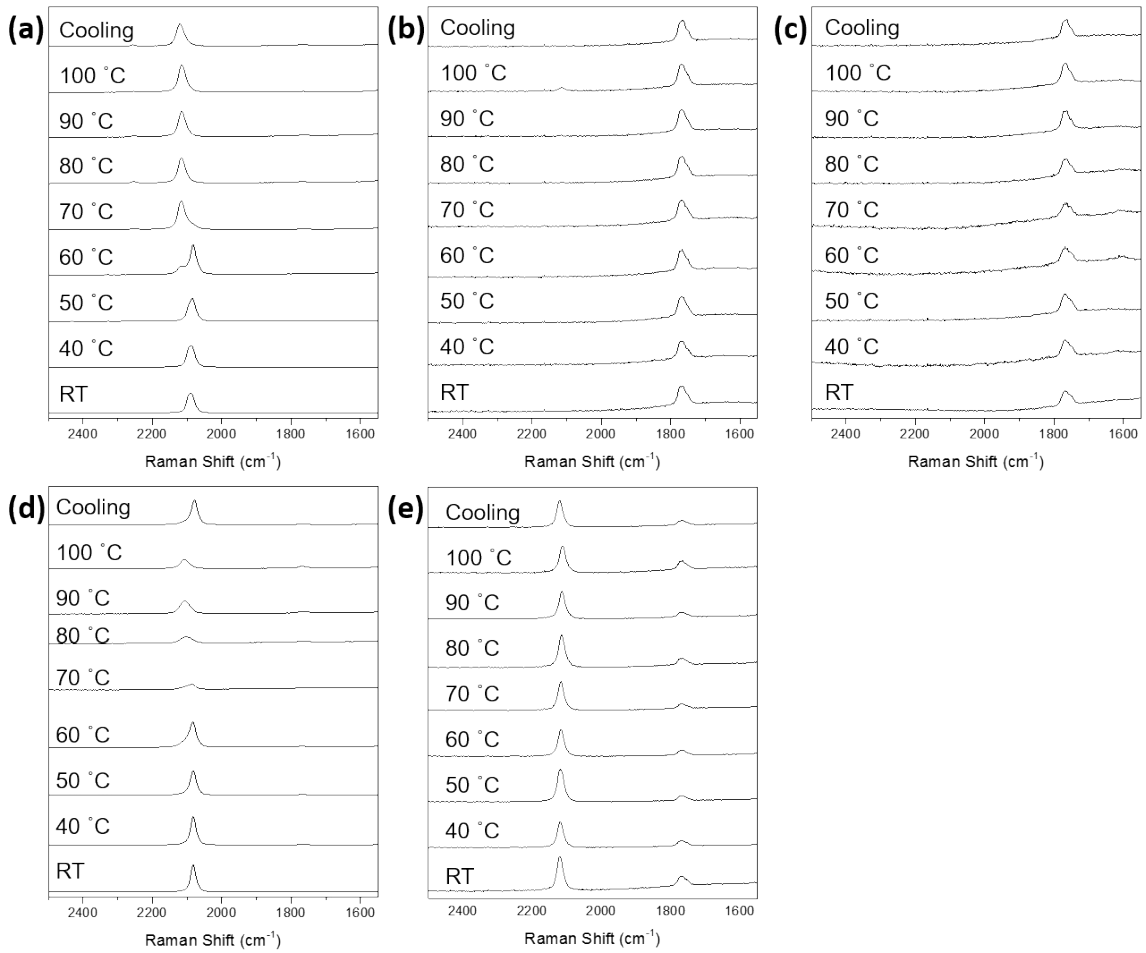
103 **Figure S6**. (a) UV-Vis spectra and (b) Time-resolved development of maximum absorption at

104 640 nm of kinetics of polymerization.



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106 **Figure S7**. Temperature dependent Raman spectra of film (a) PDA/PLA, (b) PLLA-PDA/PLA,

107 (c) 4PLLA-4PDA/PLA, (d) 4BzD-8PLLA-8PDA/PLA and (e) mPEI-PLLA-PDA/PLA.

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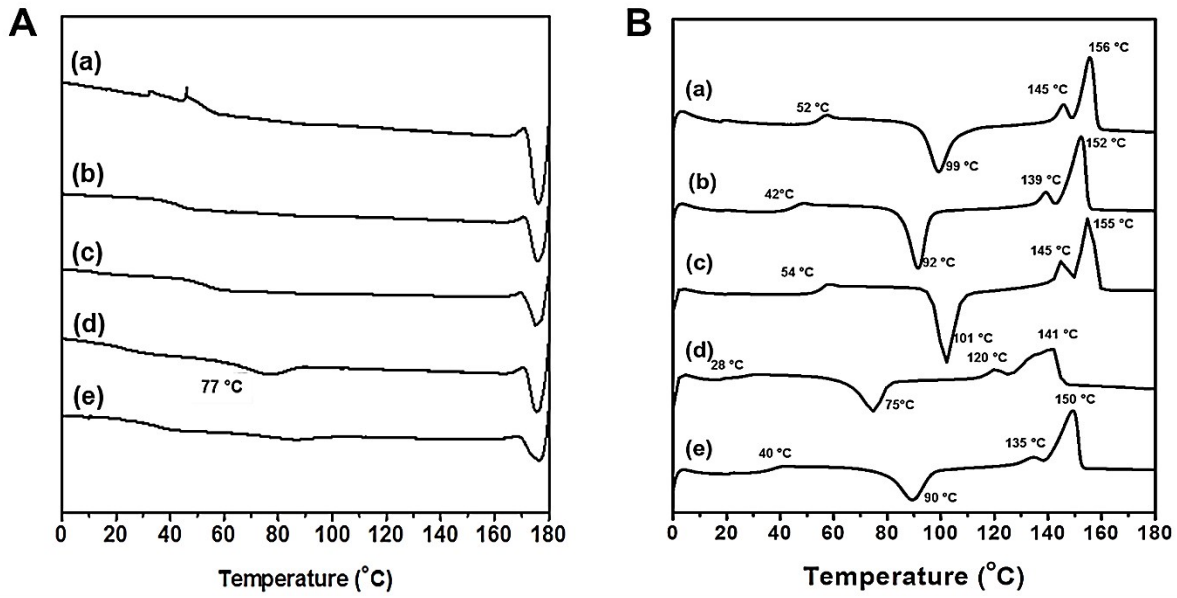

Figure S8. DSC thermogram of film (a) PDA/PLA, (b) PLLA-PDA/PLA, (c) 4PLLA-4PDA/PLA, (d) 4BzD-8PLLA-8PDA/PLA and (e) mPEI-PLLA-PDA/PLA at (A) cooling scan and (B) second heating scan.