#### **SUPPORTING INFORMATION**

#### A Library of Thermoresponsive, Coacervate-forming Biodegradable Polyesters

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#### Contents

- 1. Materials and instrumentation
- 2. Synthesis and characterization of monomers and polyesters
- 3. <sup>1</sup>H and <sup>13</sup>C NMR spectra for monomers and polyesters
- 4. Temperature controlled UV-Vis spectra of polyesters
- 5. DLS analysis of polyesters
- 6. Degradation studies of TR-iPrPE
- 7. Optical micrographs and images of polyesters coacervates
- 8. References

#### 1. MATERIALS AND INSTRUMENTATION

Materials: Succinic acid (99%), ethyl succinyl chloride (98%), isopropylamine (99%), pyrrolidine (99%), propylamine (98%), cyclopropylamine (99%), triethylamine (Et<sub>3</sub>N, 98%), diethanolamine (DEA, 99%), sodium chloride (NaCl, 99%), urea (98%), and sodium dodecyl sulfate (SDS, 98%) were purchased from Acros Organic and used as received. N,N'-diisopropylcarbodiimide (DIC, 99%) was purchased from Oakwood Chemical and used as received. 4-(dimethylamino) pyridinium 4-toluene sulfonate (DPTS) was prepared according to literature methods. (ref) Reagent grade dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was purchased from Thermo Fisher Scientific and dried by distilling over anhydrous CaH<sub>2</sub>. Reagent grade tetrahydrofuran (THF) and methanol (MeOH) were used as received from Thermo Fisher Scientific. Silica gel (40-63 µm, 230 x 400 mesh) for flash chromatography was purchased from Thermo Fisher Scientific. Deionized water was used to prepare polymer solutions unless otherwise stated.

Instrumentation: All <sup>1</sup>H and <sup>13</sup>C NMR spectra in CDCl<sub>3</sub> of the monomers and polyesters were recorded on either a Varian Mercury 300 MHz or 500 MHz spectrometer. Chemical shifts were recorded in ppm ( $\delta$ ) relative to solvent signals. Variable temperature <sup>1</sup>H NMR spectra in D<sub>2</sub>O were recorded on a Varian INOVA 400 MHz spectrometer with 15 minute equilibrations at each temperature. Glass transition temperatures (T<sub>g</sub>) of the polymers were determined using a TA Q2000 DSC with a liquid N<sub>2</sub> cooling unit and a heating/cooling rate of 10°C/min. Polyester molecular weights were analyzed on a TOSOH EcoSec HLC-8320 GPC equipped with a refractive index detector (RI) and UV detector. Separation occurred over two PSS Gram Analytical GPC Columns in series using 25 mM LiBr in DMF as eluent at a flow rate of 0.8 mL/min. The column and detector temperatures were maintained at 50°C. Molecular weights were obtained relative to PMMA standards using the RI signal. Optical microscopy was carried out on an Olympus IX81 Motorized Inverted Microscope using either Brightfield or TRITC channel filters. Turbidity measurements were carried out on a Shimadzu UV-1800 UV-VIS spectrophotometer equipped with a Shimadzu S-1700 thermoelectric single cell holder in a 1 cm quartz cell. Deionized water was used as a reference. Polyester solutions (10 mg/mL unless otherwise noted) were prepared in DI water and left at 4°C overnight to ensure complete dissolution and equilibration. Solutions were equilibrated at 0°C or 5°C until no change in transmittance was observed. Transmittance was recorded as a function of temperature at 1°C/min and a fixed 350 nm wavelength.  $T_{cp}$  was defined as the temperature at which the transmittance was 50%. DLS measurements of the homopolymer aqueous solutions (0.5 mg/mL) were preformed on a Brookhaven Inc. Laser light scattering spectrometer equipped with a temperature controlled and a solid state laser ( $\lambda = 532$  nm, detection angle: 90°). An intensity-intensity time correlation function was measured by means of a multichannel digital correlator, which was then processed using the CONTIN method to obtain the average hydrodynamic radius of the particles in solution. The solutions were filtered through a 0.45 µm PVDF filter prior to measurements. The solutions were equilibrated for 30 minutes at each temperature. Increasing the temperature far above the  $T_{cp}$  over the long duration of the experiment resulted in very turbid solutions that did not allow the laser of the Brookhaven Goniometer to fully transmit through, and experiments were only carried out while accurate scattering data could be obtained.

#### 2. SYNTHESIS AND CHARACTERIZATION OF MONOMERS AND POLYESTERS

a) Synthesis of hydroxyethylamide (HEA) monomers



HEA monomers were synthesized according the to previous literature procedure.<sup>1</sup> As a representative example, in a round bottom flask equipped with a magnetic stir bar was added methyl butyrate (5.00 mL, 43.9 mmol, 1 eq.) and DEA (9.23 g, 87.8 mmol, 2 eq.) which was heated at 80°C overnight. After removing displaced MeOH under reduced pressure, the crude compound was analyzed via TLC (10% MeOH in DCM, ninhydrin). The product was observed at  $R_f \sim 0.45$  while unreacted DEA remained at  $R_f \sim 0$ . The crude mixture was purified via silica gel flash chromatography (10-20% MeOH in CH<sub>2</sub>Cl<sub>2</sub>). The product was dried under reduced pressure to afford pure **1a** as a pale oil (5.25 g, 30.0 mmol, 65%). The **1a** monomer was characterized via NMR and IR.

**HEA 1a:** Yield = 69% (5.3 g, 30 mmol), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.93 (t, *J* = 7.4 Hz, 3H), 1.63 (sextet, *J* = 7.5 Hz, 2H), 2.35 (t, *J* = 7.6 Hz, 2H), 3.49 (dt, *J* = 11.1, 5.4 Hz, 4H), 3.76 (dt, *J* = 11.4, 5.5 Hz, 4H), 4.26 (br s, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  13.95, 18.74, 35.48, 50.53, 52.23, 60.68, 61.16, 175.47.

**HEA 1b:** Yield = 69% (5.3 g, 30 mmol), <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  1.09 (d, J = 6.7 Hz, 6H), 2.87 (dt, J = 13.4, 6.7 Hz, 1H), 3.50 (td, J = 5.1, 2.5 Hz, 4H), 3.76 (dt, J = 9.9, 5.0 Hz, 4H), 4.26 (br s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  19.64, 30.54, 50.80, 52.06, 61.07, 61.49, 179.83.

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b) Synthesis of hydroxyethylsuccinamide (HESA) monomers



Ethoxy succinamide were synthesized according to modified literature procedures.<sup>1-2</sup> As a representative example, in a round bottom flask equipped with a magnetic stir bar, pyrrolidine (3.0 mL,

36.5 mmol, 1 eq.) and Et<sub>3</sub>N (5.20 mL, 37.3 mmol, 1.02 eq.) were dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (40 mL) with magnetic stirring. The reaction was cooled to 0°C and purged with nitrogen for 15 minutes. Ethyl succinyl chloride (5.20 mL, 36.5 mmol, 1 eq.) was added dropwise via syringe and the reaction became an opaque white solution. The reaction was brought to room temperature and allowed to stir for 1 h under nitrogen. The solution was then added to DI water and extracted (3 x 40 mL CH<sub>2</sub>Cl<sub>2</sub>). The product was dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford pure **4a** as a white solid (6.98 g, 35.1 mmol, 96%). In a round bottom flask equipped with a magnetic stir bar was added **4a** (6.73 g, 33.8 mmol, 1 eq.) and DEA (7.10 g, 67.5 mmol, 2 eq.) and allowed to heat at 80°C overnight under magnetic stirring. After removing displaced EtOH under reduced pressure, the crude compound was analyzed via TLC (15% MeOH in DCM, ninhydrin). A small amount of unreacted ethoxy amide (R<sub>f</sub> ~ 0.56) was observed along with the desired compound (R<sub>f</sub> ~ 0.40). The crude mixture was purified via silica gel flash chromatography (10-20% MeOH in CH<sub>2</sub>Cl<sub>2</sub>). The product was dried under reduced pressure to afford pure HESA monomer **4b** as a pale oil (3.42 g, 13.2 mmol, 40%). HESA monomer **4b** was characterized via NMR and IR.

**1'a:** Yield = 96%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.46-0.41 (m, 2H), 0.71-0.65 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H), 2.37 (t, *J* = 6.9 Hz, 2H), 2.74-2.57 (m, 3H), 4.08 (q, *J* = 7.1 Hz, 3H), 6.19 (s, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  6.49, 14.21, 22.67, 29.65, 30.90, 60.70, 173.10.

**1'b:** Yield = 96%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.15 (t, *J* = 7.1 Hz, 3H), 1.91-1.70 (m, 4H), 2.58-2.43 (m, 4H), 3.35 (t, *J* = 6.8 Hz, 4H), 4.03 (q, *J* = 7.1 Hz, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  14.13, 24.33, 26.00, 29.09, 45.62, 46.37, 60.41, 169.65, 173.17.

**1'c:** Yield = 95%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.08 (t, *J* = 7.1 Hz, 3H), 1.21 (dt, *J* = 17.7, 7.1 Hz, 6H), 2.68-2.56 (m, 4H), 3.39-3.28 (m, *J* = 11.3, 7.1 Hz, 4H), 4.12 (q, *J* = 7.1 Hz, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  13.13, 14.24, 27.93, 29.56, 40.34, 41.86, 60.49, 76.91, 77.16, 77.41, 170.30, 173.29.

**1'd:** Yield = 97%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.06 (d, J = 6.6 Hz, 6H), 1.18 (t, 3H), 2.36 (t, J = 7.0 Hz, 2H), 2.57 (t, J = 6.8 Hz, 2H), 4.10-3.95 (m, 3H), 5.82 (br s, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  14.24, 22.76, 29.81, 31.32, 41.45, 60.68, 170.56, 173.11.

**1'e:** Yield = 98%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.89 (t, *J* = 7.4 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.49 (sextet, *J* = 7.3 Hz, 2H), 2.44 (t, *J* = 6.8 Hz, 2H), 2.64 (t, *J* = 6.8 Hz, 2H), 3.19 (q, *J* = 7.1 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 5.79 (s, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  11.35, 14.20, 22.86, 29.79, 31.14, 41.34, 60.66, 171.45, 173.11.

**HESA 2'a:** Yield = 55%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.50-0.44 (m, 2H), 0.75-0.68 (m, 2H), 2.48 (t, J = 6.4 Hz, 2H), 2.61-2.68 (m, 1H), 2.73 (t, J = 6.5 Hz, 2H), 3.53 (q, J = 5.0 Hz, 5H), 3.79 (br s, 5H), 4.03 (br s, 1H), 4.47 (br s, 1H), 6.45 (br s, 1H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  6.29, 22.63, 28.67, 31.20, 50.48, 52.13, 60.43, 173.92, 174.50.

**HESA 2'b:** Yield = 63%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.98-1.77 (m, 4H), 2.67 (q, *J* = 6.0 Hz, 4H), 3.41 (dt, *J* = 10.5, 6.8 Hz, 4H), 3.54 (dt, *J* = 15.4, 4.9 Hz, 4H), 3.78 (dd, *J* = 9.7, 4.7 Hz, 4H), 4.03 (br s, 1H), 4.78 (br s, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  24.27, 25.89, 27.71, 29.91, 45.74, 46.51, 50.59, 52.30, 60.75, 170.87, 173.86.

**HESA 2'c:** Yield = 44%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta 0.93$  (t, 3H),  $\delta 1.62$  (m, 2H),  $\delta 2.34$  (t, 2H),  $\delta 3.47$  (m, 4H),  $\delta 3.74$  (m, 4H),  $\delta 4.23$  (br, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta 12.97$ , 13.98, 28.05, 28.55, 40.47, 42.04, 50.67, 52.38, 60.82, 171.51, 174.05.

**HESA 2'd:** Yield = 55%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.04 (d, *J* = 6.5 Hz, 6H), 2.40 (t, *J* = 6.7 Hz, 2H), 2.64 (t, *J* = 6.7 Hz, 2H), 3.46 (dt, *J* = 9.3, 4.8 Hz, 4H), 3.69 (s, 5H), 3.90 (dq, *J* = 13.8, 6.8 Hz, 1H),

4.54 (br s, 1H), 4.89 (br s, 1H), 6.49 (d, J = 7.8 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  22.65, 28.73, 31.57, 41.58, 50.62, 52.24, 60.73, 171.93, 173.97.

**HESA 2'e:** Yield = 38%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.07 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 2.74-2.71 (m, 4H), 3.29-3.37 (m, 4H), 3.56 (dt, *J* = 14.9, 4.4 Hz, 4H), 3.78-3.83 (m, 4H), 4.65 (br s, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  11.47, 22.85, 28.66, 31.63, 41.53, 50.96, 52.53, 60.85, 61.23, 172.84, 174.31.

c) Synthesis of HEA polyesters



Homopolyesters were prepared according to previously established methods.<sup>1</sup> In a round bottom flask equipped with a magnetic stir bar, **1a** (1.10 g, 6.31 mmol, 1 equiv.), succinic acid (0745 mg, 6.31 mmol, 1 equiv.), and DPTS (736 mg, 2.52 mmol, 0.4 equiv.) were dissolved in dry  $CH_2Cl_2$  (4.5 mL, 1 mL / 100 mmol COOH) and purged with nitrogen for 15 minutes with stirring. This mixture was then briefly heated to reflux to homogenize the solution. The reaction was cooled to 0°C and DIC (3.0 mL, 18.9 mmol, 3 eq.) was added dropwise via syringe. The reaction was allowed to come to room temperature and stir for 24-48 h under nitrogen. The crude reaction mixture was purified via precipitation into cold MeOH. The purified polymer was dried under reduced pressure to obtain HEA polymer **2a** as a viscous transparent pale oil. The resultant polyester was characterized by GPC and NMR.

**HEA Polymer 2a:** Yield = 41%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.96 (t, *J* = 7.4 Hz, 3H), 1.66 (sextet, *J* = 7.4 Hz, 2H), 2.33 (t, *J* = 7.4 Hz, 2H), 2.62 (t, *J* = 3.2 Hz, 4H), 3.61 (q, *J* = 5.3 Hz, 4H), 4.24-4.22 (m, 4H). Urea impurity from polymerization observable at  $\delta$ 1.19 and  $\delta$ 4.01.

**HEA Polymer 2b:** Yield = 20%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.11 (d, *J* = 6.7 Hz, 6H), 1.11 (d, *J* = 6.7 Hz, 6H), 2.60 (t, *J* = 2.8 Hz, 4H), 2.60 (t, *J* = 2.8 Hz, 4H), 2.82 (septet, *J* = 13.4, 6.7 Hz, 1H), 3.65-3.57 (m, 4H), 3.65-3.57 (m, 4H), 4.22-4.21 (m, 4H), 4.22-4.21 (m, 4H). Urea impurity from polymerization observable at  $\delta$ 1.19 and  $\delta$ 4.01.

#### d) Synthesis of HESA polymers



Homopolyesters and copolyesters of various monomers with succinic acid were prepared according to previously established methods.<sup>1</sup> As a representative example, in a round bottom flask equipped with a magnetic stir bar, **2'b** (1.25 g, 4.85 mmol, 1 equiv.), succinic acid (573 mg, 4.85 mmol, 1 equiv.), and DPTS (570 mg, 1.94 mmol, 0.4 equiv.) were dissolved in dry  $CH_2Cl_2$  (4.5 mL, 1 mL / 100 mmol COOH) and purged with nitrogen for 15 minutes with magnetic stirring. This mixture was then briefly heated to reflux to homogenize the solution. The reaction was cooled to 0°C and DIC (2.28 mL, 14.6 mmol, 3 eq.) was added dropwise via syringe. The reaction was allowed to come to room temperature and stir for 24-48 h under nitrogen. Since the HESA monomers, polyesters, DPTS, DIC urea byproducts all displayed similar solubilities in common organic solvents, **3'b** was purified via dialysis against MeOH for 24 h with solvent changes at 3 h, 6 h, and 16 h. The dialysis mixture was dried under vacuum to obtain pure **3'b** polyester as a white amorphous solid. The resultant polyester was characterized by GPC and NMR.

**TR-CPPE 3'a:** Yield = 62%, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  0.47 (s, 2H), 0.70 (q, *J* = 6.1 Hz, 2H), 2.45 (s, 2H), 2.71-2.59 (m, 7H), 3.67-3.58 (m, 4H), 4.23 (dt, *J* = 16.0, 5.3 Hz, 4H), 6.67 (s, 1H).

**TR-PyrPE 3'b:** Yield = 66%, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  1.89 (dquintet, J = 55.3, 6.8 Hz, 4H), 2.65-2.59 (m, 5H), 2.71 (t, J = 6.5 Hz, 2H), 3.48-3.41 (m, 4H), 3.65 (dt, J = 47.5, 5.6 Hz, 4H), 4.28-4.20 (m, 4H).

**TR-DEPE 3'c:** Yield = 64%, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  1.14 (dt, *J* = 55.9, 7.1 Hz, 6H), 2.70-2.60 (m, 7H), 3.35 (qd, *J* = 7.1, 2.3 Hz, 4H), 3.65 (dt, *J* = 48.3, 5.6 Hz, 4H), 4.23 (dt, *J* = 26.0, 5.2 Hz, 4H).

**TR-iPrPE 3'd:** Yield = 53%, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.12 (d, *J* = 6.6 Hz, 6H), 2.47 (t, *J* = 6.6 Hz, 2H), 2.64-2.59 (m, 4H), 2.71-2.69 (t, 2H), 3.59 (t, *J* = 4.9 Hz, 2H), 3.66 (t, *J* = 5.4 Hz, 2H), 4.01 (dq, *J* = 13.0, 6.5 Hz, 1H), 4.23 (dt, *J* = 11.3, 5.5 Hz, 4H), 6.24-6.14 (m, 1H).

**TR-nPrPE 3'e:** Yield = 75%, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  0.90 (t, *J* = 7.4 Hz, 3H), 1.49 (q, *J* = 7.3 Hz, 2H), 2.50 (t, *J* = 6.0 Hz, 2H), 2.63-2.59 (m, 4H), 2.71 (t, *J* = 5.4 Hz, 2H), 3.16 (q, *J* = 6.6 Hz, 2H), 3.67-3.59 (m, 4H), 4.23 (dt, *J* = 12.6, 6.0 Hz, 4H), 6.41 (s, 1H).

## 3. <u><sup>1</sup>H AND <sup>13</sup>C NMR SPECTRA FOR MONOMERS AND POLYESTERS</u>

## <sup>1</sup>H NMR of **1a** in CDCl<sub>3</sub>



ppm 150 100 50 0



## <sup>1</sup>H NMR of **2a** in CDCl<sub>3</sub>



<sup>1</sup>H NMR of **2b** in CDCl<sub>3</sub>



## <sup>1</sup>H NMR of **1'a** in CDCl<sub>3</sub>



<sup>13</sup>C NMR of **1'a** in CDCl<sub>3</sub>



## <sup>1</sup>H NMR of **1'b** in CDCl<sub>3</sub>



<sup>13</sup>C NMR of **1'b** in CDCl<sub>3</sub>



## <sup>1</sup>H NMR of **1'c** in CDCl<sub>3</sub>



## <sup>1</sup>H NMR of **1'd** in CDCl<sub>3</sub>





## <sup>1</sup>H NMR of **1'e** in CDCl<sub>3</sub>



## <sup>1</sup>H NMR of **2'a** in CDCl<sub>3</sub>



<sup>13</sup>C NMR of **2'a** in CDCl<sub>3</sub>



## <sup>1</sup>H NMR of **2'b** in CDCl<sub>3</sub>



<sup>13</sup>C NMR of **2'b** in CDCl<sub>3</sub>



## <sup>1</sup>H NMR of **2'c** in CDCl<sub>3</sub>



<sup>13</sup>C NMR of **2'c** in CDCl<sub>3</sub>



## <sup>1</sup>H NMR of **2'd** in CDCl<sub>3</sub>





## <sup>1</sup>H NMR of **2'e** in CDCl<sub>3</sub>



<sup>13</sup>C NMR of **2'e** in CDCl<sub>3</sub>



#### <sup>1</sup>H NMR of **3'a (TR-CPPE)** in CDCl<sub>3</sub>



## <sup>1</sup>H NMR of **3'c (TR-DEPE)** in CDCl<sub>3</sub>



# <sup>1</sup>H NMR of **3'e (TR-nPrPE)** in CDCl<sub>3</sub>



# <sup>1</sup>H VT NMR of **3'c (TR-DEPE)** in $D_2O$



<sup>1</sup>H VT NMR of **3'd (TR-iPrPE)** in D<sub>2</sub>O



UV-Vis Spectra of Polymer Concentration Effect



**Figure S1.** Temp controlled UV-Vis spectra of different wt% **3'b** (**TR-PyrPE**) solutions in DI H<sub>2</sub>O. Heating rate: 1°C/min, 350 nm.



Figure S2. Temp controlled UV-Vis spectra of different wt% 3'c (TR-DEPE) solutions in DI H<sub>2</sub>O. Heating rate:  $1^{\circ}C/min$ , 350 nm.



Figure S3. Temp controlled UV-Vis spectra of different wt% 3'd (TR-iPrPE) solutions in DI H<sub>2</sub>O. Heating rate:  $1^{\circ}C/min$ , 350 nm.

UV-Vis Spectra of Molecular Weight Effect



**Figure S4.** Temp controlled UV-Vis spectra of different  $M_n$  **3'b** (**TR-PyrPE**) solutions (10 mg/mL) in DI H<sub>2</sub>O. Heating rate: 1°C/min, 350 nm.



Figure S5. Temp controlled UV-Vis spectra of different  $M_n$  3'd (TR-DEPE) solutions (10 mg/mL) in DI H<sub>2</sub>O. Heating rate: 1°C/min, 350 nm.



**Figure S6.** Temp controlled UV-Vis spectra of different  $M_n$  **3'c (TR-iPrPE)** solutions (10 mg/mL) in DI H<sub>2</sub>O. Heating rate: 1°C/min, 350 nm.



**Figure S7.** Temp controlled UV-Vis spectra of **3'b** (**TR-PyrPE**) solutions (10 mg/mL) in DI H<sub>2</sub>O containing varying concentrations of NaCl. Heating rate:  $1^{\circ}C/min$ , 350 nm.



**Figure S8.** Temp controlled UV-Vis spectra of **3'c** (**TR-DEPE**) solutions (10 mg/mL) in DI H<sub>2</sub>O containing varying concentrations of NaCl. Heating rate:  $1^{\circ}C/min$ , 350 nm.

UV-Vis Spectra of SDS Concentration Effect



**Figure S9.** Temp controlled UV-Vis spectra of **3'a** (**TR-CPPE**) solutions (10 mg/mL) in DI H<sub>2</sub>O containing varying concentrations of SDS. Heating rate:  $1^{\circ}C/min$ , 350 nm.



**Figure S10.** Temp controlled UV-Vis spectra of **3'b** (**TR-PyrPE**) solutions (10 mg/mL) in DI H<sub>2</sub>O containing varying concentrations of SDS. Heating rate: 1°C/min, 350 nm.



**Figure S11.** Temp controlled UV-Vis spectra of **3'c** (**TR-DEPE**) solutions (10 mg/mL) in DI H<sub>2</sub>O containing varying concentrations of SDS. Heating rate:  $1^{\circ}$ C/min, 350 nm.



**Figure S12.** Temp controlled UV-Vis spectra of **3'd (TR-iPrPE)** solutions (10 mg/mL) in DI H<sub>2</sub>O containing varying concentrations of SDS. Heating rate: 1°C/min, 350 nm.



**Figure S13** Temp controlled UV-Vis spectra of **3'e** (**TR-nPrPE**) solutions (10 mg/mL) in DI H<sub>2</sub>O containing varying concentrations of SDS. Heating rate:  $1^{\circ}$ C/min, 350 nm.





**Figure S14.** Temp controlled UV-Vis spectra of **3'a** (**TR-CPPE**) solutions (10 mg/mL) in DI H<sub>2</sub>O containing varying concentrations of urea. Heating rate:  $1^{\circ}$ C/min, 350 nm.



Figure S15. Temp controlled UV-Vis spectra of 3'b (TR-PyrPE) solutions (10 mg/mL) in DI H<sub>2</sub>O containing varying concentrations of urea. Heating rate:  $1^{\circ}$ C/min, 350 nm.



**Figure S15.** Temp controlled UV-Vis spectra of **3'c** (**TR-DEPE**) solutions (10 mg/mL) in DI H<sub>2</sub>O containing varying concentrations of urea. Heating rate:  $1^{\circ}$ C/min, 350 nm.



**Figure S16.** Temp controlled UV-Vis spectra of **3'd** (**TR-iPrPE**) solutions (10 mg/mL) in DI H<sub>2</sub>O containing varying concentrations of urea. Heating rate:  $1^{\circ}$ C/min, 350 nm.



**Figure S17.** Temp controlled UV-Vis spectra of **3'e** (**TR-nPrPE**) solutions (10 mg/mL) in DI H<sub>2</sub>O containing varying concentrations of urea. Heating rate:  $1^{\circ}$ C/min, 350 nm.



**Figure S18.** Temp controlled UV-Vis spectra of **TR-(iPr-co-Pyr)PE** copolymer solutions (10 mg/mL) in DI H<sub>2</sub>O. Heating rate: 1°C/min, 350 nm.

Polymer composition (iPr : Pyr)	Mn (kDa)	Đ	CP (°C)
100:0	56.6	1.6	7.2
75:25	52.2	1.4	7.9
50:50	56.0	1.4	9.5
25:75	55.0	1.4	13.1
0:100	54.2	1.5	15.8

#### 5. DLS ANALYSIS OF POLYMERS

#### DLS of 3'b (TR-PyrPE) in D<sub>2</sub>O



DLS of 3'c (TR-DEPE) in D<sub>2</sub>O



#### DLS of 3'd (TR-iPrPE) in D<sub>2</sub>O



#### 6. DEGRADATION STUDIES OF 3'c (TR-DEPE)



Normalized GPC traces of TR-DEPE at various days of incubation at 37°C. Traces are for "Sample 1."

Day	Sample 1	Sample 2	Sample 3	Avg $M_n$	Avg $M_n$ Remain
	(kDa)	(kDa)	(kDa)	(kDa)	(%)
0	72.7	72.7	72.7	72.7	100.0
1	58.9	56.9	59.9	58.6	80.6
4	38.5	36.8	36.8	37.4	51.4
7	27.2	27.3	25.6	26.7	36.7

Table S1. Degradation Analysis of TR-DEPE



**Figure S19.** Solution containing 1 wt% TR-PE (75 : 25 TR-(Pyr-co-iPr)PE), 5 drops 50  $\mu$ M Nile Red in DMSO added to both tubes. Brought to RT w/ water bath for 1 min, photographed, centrifuged 3600 RPM for 5 mins.

#### 8. <u>REFERENCES</u>

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#### 7. OPTICAL MICROGRAPHS OF POLYMER COACERVATES