

Supporting Information

The Effect of Structure on Thermal and Thermoresponsive Properties of N-Substituted Polyesters

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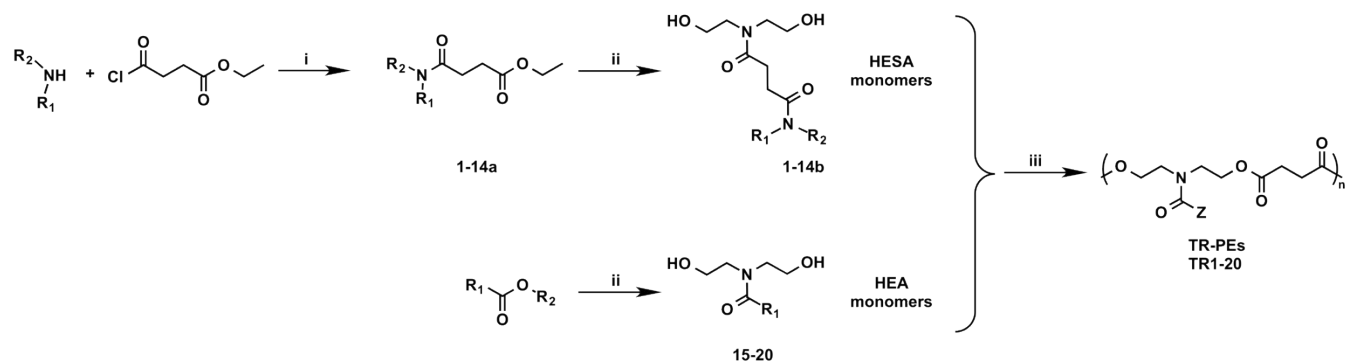
Table S1. T_{cp} Data corresponding to polymers in Figure 4.

Polymer	MW (kDa)	T_{cp} (°C)	Polymer	MW (kDa)	T_{cp} (°C)
TR7	7.3	24.3	TR11	15.9	45.3
	10.2	20		20.4	42.1
	11.3	14.7		23.5	39.4
	19.5	13.2		29.3	37.6
	23.1	11.6		30.3	37.8
	56.6	7.8		40.8	34.9
TR8	9.3	25.9	TR12	19.6	52.4
	10.8	21.5		20.3	51.7
	12.5	19.7		23.6	47.1
	14.1	21.3		29.4	40.2
	15.1	18.1		31.2	43.4
	17.7	17.3		33	42.4
	17.8	17.1		42.4	40.2
	47.1	13.1	TR13	23.9	60.2
	56.5	11.9		45.6	53.5
	63.2	11.9		46.7	51.8
	72.7	10.4		54.1	51.5
TR9	7.6	36.8	54.7	51.6	
	15.3	25.6	57.3	50.6	
	17.8	22.2	105.5	48.4	

	23.2	21.9		105.7	48.4
	28.4	18.8		107.8	49.4
	39.2	15.5		116.7	50.7
	54.2	15.8		133.5	48.1
TR10	19.3	26.7	TR14	43.7	77.2
	20.9	25.1	TR19	16.9	31.2
	20.9	25.6		20.4	27.9
	37.7	21		46.2	20.4
	48.5	20.1		75.4	15.6
	55.3	19	TR20	22.9	60.6
	61.1	18.9		23.1	62
		32.8		60.8	
		36		61.2	

I. Synthesis of Monomers and Polymers

Scheme S1. Synthetic route for preparation of monomers and polyesters^a



^aReagents and conditions: (i) Et₃N, CH₂Cl₂, 0 °C to room-temperature, 1 h. (ii) DEA, neat, 80 °C, vacuum, 16 h. (iii) Et₃N, MeOH, 60 °C microwave, 2 h. (iii) SA, DIC, DPTS, CH₂Cl₂, 0 °C to room-temperature, 48 h.

General Procedure for Synthesis of *N*-Substituted Diol Monomers

The synthetic procedures used to synthesize the *N*-substituted diol monomers are described in this section using a modified version of the previous literature procedure.^{28, 38} Synthesis of *N*¹-cyclopropyl-*N*⁴,*N*⁴-bis(2-hydroxyethyl)succinamide (**cPrA**, **1b**), *N*¹,*N*¹-bis(2-hydroxyethyl)-*N*⁴-propylsuccinamide (**nPrA**, **2b**), *N*¹,*N*¹-bis(2-hydroxyethyl)-*N*⁴-(prop-2-yn-1-yl)succinamide (**propargylA**, **3b**), *N*,*N*-bis(2-hydroxyethyl)-4-oxo-4-(pyrrolidin-1-yl)butanamide (**PyrA**, **4b**), *N*¹,*N*¹-bis(2-hydroxyethyl)-*N*⁴-isopropylsuccinamide (**iPrA**, **7b**), *N*¹,*N*¹-diethyl-*N*⁴,*N*⁴-bis(2-hydroxyethyl)succinamide (**dEtA**, **8b**),

*N*¹,*N*¹-bis(2-hydroxyethyl)-*N*⁴,*N*⁴-bis(2-methoxyethyl)succinamide (**bMoEtA**, **13b**), *N,N*-bis(2-hydroxyethyl)butyramide (**nPr**, **15**), *N,N*-bis(2-hydroxyethyl)isobutyramide (**iPr**, **16**), *N,N*-bis(2-hydroxyethyl)propionamide (**Et**, **17**), and was undertaken according to previous literature procedures.²⁸

Ethyl 4-oxo-4-(pyrrolidin-1-yl)butanoate (1a): Yield = 96%. ¹H NMR (300 MHz, CDCl₃): δ 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); ¹³C NMR (126 MHz, CDCl₃): δ 14.13, 24.33, 26.00, 29.09, 45.62, 46.37, 60.41, 169.65, 173.17.

*N*¹-cyclopropyl-*N*⁴,*N*⁴-bis(2-hydroxyethyl)succinamide (**cPrA**, **1b**): Yield = 82.6%. ¹H NMR (300 MHz, CDCl₃): δ 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). ¹³C NMR (126 MHz, CDCl₃): δ 6.29, 22.63, 28.67, 31.20, 50.48, 52.13, 60.43, 173.92, 174.50.

Ethyl 4-oxo-4-(propylamino)butanoate (2a): Yield = 98.4%. ¹H NMR (300 MHz, CDCl₃): δ 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); ¹³C NMR (126 MHz, CDCl₃): δ 11.35, 14.20, 22.86, 29.79, 31.14, 41.34, 60.66, 171.45, 173.11.

*N*¹,*N*¹-bis(2-hydroxyethyl)-*N*⁴-propylsuccinamide (**nPrA**, **2b**): Yield = 38%. ¹H NMR (300 MHz, CDCl₃): δ 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); ¹³C NMR (126 MHz, CDCl₃): δ 11.47, 22.85, 28.66, 31.63, 41.53, 50.96, 52.53, 60.85, 61.23, 172.84, 174.31.

Ethyl 4-oxo-4-(piperidin-1-yl)butanoate (4a): Yield = 91.8%. ¹H NMR (300 MHz, CDCl₃): δ 1.25 (d, *J* = 14.3 Hz, 3H), 1.58 (dq, *J* = 18.7, 5.7 Hz, 6H), 2.63 (dd, *J* = 4.5, 3.4 Hz, 4H), 3.41 (t, *J* = 5.3 Hz, 2H), 3.54 (t, *J* = 5.5 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 13.93, 24.29, 25.29, 26.11, 27.66, 29.20, 42.56, 46.10, 60.10, 169.07, 172.87.

N,N-bis(2-hydroxyethyl)-4-oxo-4-(piperidin-1-yl)butanamide (**PPDA**, **4b**): Yield = 52.4%. ¹H NMR (500 MHz, CDCl₃): δ 1.63-1.51 (m, 6H), 2.72 (dd, *J* = 16.8, 5.5 Hz, 4H), 3.43 (d, *J* = 5.1 Hz, 2H), 3.61-3.49 (m, 6H), 3.83 (dd, *J* = 14.7, 3.6 Hz, 4H), 4.64 (s, 1H); ¹³C NMR (126 MHz, CDCl₃): δ 24.57, 25.61, 26.37, 27.94, 29.06, 43.17, 46.62, 50.93, 52.69, 61.18, 61.30, 170.65, 174.65.

Ethyl 4-(dibutylamino)-4-oxobutanoate (5a): Yield = 96.5%. ¹H NMR (300 MHz, CDCl₃): δ 0.93 (dt, *J* = 13.2, 7.3 Hz, 6H), 1.37-1.23 (m, 8H), 1.62-1.44 (m, 4H), 2.69-2.57 (m, 4H), 3.27 (dt, *J* = 18.4, 7.7 Hz, 4H), 4.14 (q, *J* = 7.1 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 13.62, 13.67, 13.99, 19.95, 20.06, 27.77, 29.37, 29.73, 30.88, 45.70, 47.42, 60.21, 170.45, 172.99.

*N*¹,*N*¹-dibutyl-*N*⁴,*N*⁴-bis(2-hydroxyethyl)succinamide (**dnBuA**, **5b**): Yield = 48.8%. ¹H NMR (500 MHz, CDCl₃): δ 0.93 (dt, *J* = 25.9, 7.3 Hz, 6H), 1.31 (dq, *J* = 32.2, 7.5 Hz, 4H), 1.47 (dt, *J* = 14.9, 7.5 Hz, 2H), 1.58 (dt, *J* = 15.1, 7.6 Hz, 2H), 2.74 (dd, *J* = 19.5, 6.0 Hz, 4H), 3.26 (dt, *J* = 13.8, 7.2 Hz, 4H), 3.58 (dt, *J* = 25.2, 4.6 Hz, 4H), 3.68 (s, 1H), 3.83 (d, *J* = 19.6 Hz, 4H), 4.61-4.57 (m, 1H); ¹³C NMR (126 MHz, CDCl₃): δ 13.93, 14.00, 20.31, 27.99, 29.22, 29.96, 30.95, 46.14, 47.93, 51.04, 52.82, 61.24, 61.30, 172.04, 174.70.

Ethyl 4-(heptylamino)-4-oxobutanoate (6a): Yield = 96.5%. ¹H NMR (300 MHz, CDCl₃): δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.28-1.23 (m, 11H), 1.48 (t, *J* = 6.3 Hz, 2H), 2.44 (t, *J* = 6.8 Hz, 2H), 2.64 (q, *J* = 6.6 Hz, 2H), 3.23 (td, *J* = 7.1, 5.9 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 5.63 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 13.98, 14.12, 22.53, 26.84, 28.93, 29.56, 29.72, 31.02, 31.71, 39.61, 60.55, 171.36, 173.02.

*N*¹-heptyl-*N*⁴,*N*⁴-bis(2-hydroxyethyl)succinamide (**HepA**, **6b**): Yield = 21.0%. ¹H NMR (500 MHz, CDCl₃): δ 0.87 (t, *J* = 6.7 Hz, 3H), 1.28 (s, 8H), 1.46 (t, *J* = 6.5 Hz, 2H), 2.54 (t, *J* = 6.4 Hz, 2H), 2.73 (t, *J* = 6.4 Hz, 2H), 3.19 (q, *J* = 6.6 Hz, 2H), 3.55 (t, *J* = 5.0 Hz, 4H), 3.80 (s, 5H), 4.31 (s, 1H), 6.04 (s, 1H); ¹³C NMR (126 MHz, CDCl₃): δ 14.19, 22.72, 27.00, 28.60, 29.08, 29.64, 31.69, 31.88, 39.89, 50.99, 52.55, 60.93, 61.34, 172.69, 174.35.

Ethyl 4-(isopropylamino)-4-oxobutanoate (**7a**): Yield = 93.9%. ¹H NMR (300 MHz, CDCl₃): δ 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); ¹³C NMR (126 MHz, CDCl₃): δ 14.24, 22.76, 29.81, 31.32, 41.45, 60.68, 170.56, 173.11.

*N*¹,*N*¹-bis(2-hydroxyethyl)-*N*⁴-isopropylsuccinamide (**iPrA**, **7b**): Yield = 55%. ¹H NMR (300 MHz, CDCl₃): δ 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); ¹³C NMR (126 MHz, CDCl₃): δ 22.65, 28.73, 31.57, 41.58, 50.62, 52.24, 60.73, 171.93, 173.97.

Ethyl 4-(diethylamino)-4-oxobutanoate (**8a**): Yield = 96%. ¹H NMR (300 MHz, CDCl₃): δ 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); ¹³C NMR (126 MHz, CDCl₃): δ 13.13, 14.24, 27.93, 29.56, 40.34, 41.86, 60.49, 76.91, 77.16, 77.41, 170.30, 173.29.

*N*¹,*N*¹-diethyl-*N*⁴,*N*⁴-bis(2-hydroxyethyl)succinamide (**dEtA**, **8b**): Yield = 44%. ¹H NMR (300 MHz, CDCl₃): δ 0.93 (t, 3H), δ 1.62 (m, 2H), δ 2.34 (t, 2H), δ 3.47 (m, 4H), δ 3.74 (m, 4H), δ 4.23 (br, 2H); ¹³C NMR (126 MHz, CDCl₃): δ 12.97, 13.98, 28.05, 28.55, 40.47, 42.04, 50.67, 52.38, 60.82, 171.51, 174.05.

Ethyl 4-oxo-4-(pyrrolidin-1-yl)butanoate (**9a**): Yield = 96%. ¹H NMR (300 MHz, CDCl₃): δ 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); ¹³C NMR (126 MHz, CDCl₃): δ 14.13, 24.33, 26.00, 29.09, 45.62, 46.37, 60.41, 169.65, 173.17.

N,N-bis(2-hydroxyethyl)-4-oxo-4-(pyrrolidin-1-yl)butanamide (**Pyra**, **9b**): Yield = 63%. ¹H NMR (300 MHz, CDCl₃): δ 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); ¹³C NMR (126 MHz, CDCl₃): δ 24.27, 25.89, 27.71, 29.91, 45.74, 46.51, 50.59, 52.30, 60.75, 170.87, 173.86.

Ethyl 4-oxo-4-(((tetrahydrofuran-2-yl)methyl)amino)butanoate (**10a**): Yield = 91.7%. ¹H NMR (300 MHz, CDCl₃): δ 1.25 (t, *J* = 7.1 Hz, 3H), 1.58-1.50 (m, 1H), 2.01-1.84 (m, 3H), 2.48 (t, *J* = 6.7 Hz, 2H), 2.68-2.61 (m, 2H), 3.14 (ddd, *J* = 13.8, 7.4, 4.9 Hz, 1H), 3.57 (ddd, *J* = 13.8, 6.5, 3.4 Hz, 1H), 3.78-3.70 (m, 1H), 3.87-3.82 (m, 1H), 3.97-3.89 (m, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 5.94 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 14.10, 25.74, 28.54, 29.55, 30.83, 43.17, 60.49, 67.95, 77.70, 171.49, 172.82.

*N*¹,*N*¹-bis(2-hydroxyethyl)-*N*⁴-((tetrahydrofuran-2-yl)methyl)succinamide (**THFA**, **10b**): Yield = 48.3%. ¹H NMR (300 MHz; CDCl₃): δ 2.71-2.67 (m, 2H), 2.87-2.83 (m, 2H), 3.32 (d, *J* = 10.1 Hz, 6H), 3.61-3.44 (m, 12H), 3.83 (dt, *J* = 9.0, 4.6 Hz, 4H); ¹³C NMR (75 MHz, CDCl₃): δ 25.71, 28.64, 28.67, 31.27, 43.33, 50.42, 52.04, 60.46, 60.61, 67.99, 77.76, 172.95, 173.72.

Ethyl 4-((2-ethoxyethyl)amino)-4-oxobutanoate (**11a**): Yield = 73.3%. ¹H NMR (500 MHz, CDCl₃): δ 1.23 (dt, *J* = 25.0, 7.1 Hz, 6H), 2.48 (t, *J* = 6.9 Hz, 2H), 2.66 (t, *J* = 6.9 Hz, 2H), 3.52-3.42 (m, 6H), 4.14 (q, *J* = 7.1 Hz, 2H), 5.97 (s, 1H). ¹³C NMR (126 MHz, CDCl₃): δ 14.33, 15.26, 29.75, 31.19, 39.54, 60.79, 66.57, 69.14, 171.49, 173.06.

*N*¹-(2-ethoxyethyl)-*N*⁴,*N*⁴-bis(2-hydroxyethyl)succinamide (**EOEtA**, **11b**): Yield = 50.4%. ¹H NMR (500 MHz, CDCl₃): δ 1.20 (t, *J* = 7.0 Hz, 3H), 2.60 (t, *J* = 6.3 Hz, 2H), 2.73 (dd, *J* = 7.4, 5.3 Hz, 2H), 3.41 (quintet,

$J = 5.1$ Hz, 2H), 3.49 (dt, $J = 13.0, 6.3$ Hz, 4H), 3.55 (q, $J = 4.2$ Hz, 4H), 3.73 (s, 1H), 3.82 (s, 4H), 4.25 (s, 1H), 6.26 (s, 1H); ^{13}C NMR (126 MHz, CDCl_3): δ 15.23, 28.43, 31.57, 39.55, 50.96, 52.59, 61.29, 66.54, 172.79, 174.25.

Ethyl 4-morpholino-4-oxobutanoate (12a): Yield = 91.3%. ^1H NMR (300 MHz, CDCl_3): δ 1.29-1.24 (m, 3H), 2.70-2.58 (m, 4H), 3.49 (t, $J = 4.7$ Hz, 2H), 3.63 (s, 2H), 3.67 (t, $J = 4.5$ Hz, 4H), 4.15 (q, $J = 7.1$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 14.17, 27.68, 29.22, 42.07, 45.72, 60.53, 66.51, 66.82, 169.91, 172.97.

N,N-bis(2-hydroxyethyl)-4-morpholino-4-oxobutanamide (MorA, 12b): Yield = 86.1%. ^1H NMR (500 MHz, CDCl_3): δ 2.73 (s, 4H), 3.50 (t, $J = 4.8$ Hz, 2H), 3.57 (dq, $J = 15.3, 5.1$ Hz, 6H), 3.66 (dt, $J = 18.2, 4.7$ Hz, 4H), 3.82 (dt, $J = 13.6, 4.8$ Hz, 4H), 4.27 (s, 1H); ^{13}C NMR (126 MHz, CDCl_3): δ 27.84, 28.85, 42.35, 45.94, 50.85, 52.60, 61.16, 61.44, 66.59, 66.91, 171.25, 174.43.

Ethyl 4-(bis(2-methoxyethyl)amino)-4-oxobutanoate (13a): Yield = 85.7%. ^1H NMR (300 MHz; CDCl_3): δ 1.25 (t, $J = 7.1$ Hz, 3H), 2.73-2.60 (m, 4H), 3.32 (d, $J = 6.9$ Hz, 6H), 3.57-3.50 (m, 9H), 4.13 (q, $J = 7.1$ Hz, 2H). ^{13}C NMR (126 MHz; CDCl_3): δ 14.13, 28.00, 29.45, 46.43, 48.65, 58.69, 58.98, 60.35, 70.66, 71.10, 171.70, 173.14

Nⁱ,Nⁱ-bis(2-hydroxyethyl)-N⁴,N⁴-bis(2-methoxyethyl)succinamide (bMoEtA, 13b): Yield = 41%. ^1H NMR (300 MHz; CDCl_3): δ 2.71-2.67 (m, 2H), 2.87-2.83 (m, 2H), 3.32 (d, $J = 10.1$ Hz, 6H), 3.61-3.44 (m, 12H), 3.83 (dt, $J = 9.0, 4.6$ Hz, 4H); ^{13}C NMR (126 MHz; CDCl_3): δ 14.13, 28.00, 29.45, 46.43, 48.65, 58.69, 58.98, 60.35, 70.66, 71.10, 171.70, 173.14.

Ethyl 4-((2-methoxyethyl)amino)-4-oxobutanoate (14a): Yield = 94.2%. ^1H NMR (300 MHz; CDCl_3): δ 1.25 (t, $J = 7.1$ Hz, 3H), 2.47 (t, $J = 7.0$ Hz, 2H), 2.64 (q, $J = 6.8$ Hz, 2H), 3.35 (s, 3H), 3.44-3.44 (m, 4H), 4.14 (q, $J = 7.1$ Hz, 2H), 5.96 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 14.14, 29.58, 30.89, 39.22, 58.64, 60.57, 71.15, 171.51, 172.89.

Nⁱ,Nⁱ-bis(2-hydroxyethyl)-N⁴-(2-methoxyethyl)succinamide (MoEtA, 14b): Yield = 69.8%. ^1H NMR (500 MHz; CDCl_3): δ 2.61 (t, $J = 6.3$ Hz, 2H), 2.74 (dd, $J = 7.4, 5.4$ Hz, 2H), 3.36 (s, 3H), 3.42 (dt, $J = 10.4, 5.3$ Hz, 4H), 3.56 (s, 4H), 3.70 (s, 1H), 3.83 (t, $J = 4.6$ Hz, 4H), 4.19 (s, 1H), 6.28 (s, 1H); ^{13}C NMR (126 MHz, CDCl_3): δ 28.51, 31.57, 39.37, 50.97, 52.57, 58.81, 61.02, 61.31, 71.23, 172.85, 174.24.

N,N-bis(2-hydroxyethyl)butyramide (nPr, 15): Yield = 65%. ^1H NMR (300 MHz, CDCl_3): δ 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); ^{13}C NMR (126 MHz, CDCl_3): δ 13.95, 18.74, 35.48, 50.53, 52.23, 60.68, 61.16, 175.47.

N,N-bis(2-hydroxyethyl)isobutyramide (iPr, 16): Yield = 69%. ^1H NMR (CDCl_3 , 300 MHz) δ 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). ^{13}C NMR (126 MHz, CDCl_3): δ 19.64, 30.54, 50.80, 52.06, 61.07, 61.49, 179.83.

N,N-bis(2-hydroxyethyl)acetamide (Me, 18): Yield = 61.5%. ^1H NMR (300 MHz; CDCl_3): δ 2.16 (s, 3H), 3.57-3.48 (m, 6H), 3.87-3.78 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3): δ 21.84, 50.04, 52.87, 60.20, 60.56, 172.91.

N,N-bis(2-hydroxyethyl)-2-methoxyacetamide (MoMe, 19): Yield = 80.7%. ^1H NMR (300 MHz, CDCl_3): δ 3.44 (s, 3H), 3.47 (t, $J = 5.1$ Hz, 2H), 3.56 (t, $J = 5.0$ Hz, 2H), 3.78 (t, $J = 5.1$ Hz, 2H), 3.87 (t, $J = 5.0$ Hz, 2H), 4.19 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 49.92, 50.86, 59.14, 60.01, 60.36, 71.01, 171.06.

N,N-bis(2-hydroxyethyl)-3-methoxypropanamide (**MoEt, 20**): Yield = 92.6%. ¹H NMR (300 MHz; CDCl₃): δ 2.67 (t, *J* = 6.2 Hz, 2H), 3.34 (s, 3H), 3.54 (q, *J* = 5.0 Hz, 4H), 3.70 (t, *J* = 6.2 Hz, 2H), 3.78 (dt, *J* = 16.8, 5.1 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 33.65, 50.43, 52.17, 58.81, 60.54, 60.84, 68.82, 172.96.

General Procedure for Polyesterification of *N*-Substituted Diol Monomers

Carbodiimide-mediated polyesterification was used to generate thermoresponsive poly(ester)s (TR-PEs) from *N*-substituted diols. This route allows for the generation of high molecular weight PEs bearing sensitive functional groups that might not be possible using other polyesterification methods. In a general reaction, a equimolar ratio of diol and diacid were taken into flask containing a small amount of 4-(dimethylamino) pyridinium 4-toluene sulfonate (DPTS) and dry CH₂Cl₂. The mixture was then cooled and *N,N'*-diisopropylcarbodiimide (DIC) was added dropwise and allowed to stir at room-temperature for 1 – 4 days. Detailed synthetic procedures are described below. Polyesters were prepared according to previously established methods using room-temperature carbodiimide mediated polymerization.²⁸ Note: After filtering off diisopropyl urea byproduct, the HESA-based polyesters (**TR1-14**) were purified via dialysis against MeOH. HEA-based polyesters (**TR15-20**) were purified by precipitation (2x) into cold MeOH.

TR-cPrAPE (TR1): Recovered = 1.74 g, *M_n* = 25.5 kDa, *D_M* = 1.66, *T_g* = 14 °C, *T_{deg}* = 274 °C. ¹H NMR (500 MHz, CDCl₃): δ 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-nPrAPE (TR2): Recovered = 2.11 g, *M_n* = 29.1 kDa, *D_M* = 1.52, *T_g* = 5 °C, *T_{deg}* = 271 °C. ¹H NMR (500 MHz, CDCl₃): δ 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).

TR-PropargylAPE (TR3): Recovered = 445 mg, *M_n* = 12.9 kDa, *D_M* = 1.33, *T_g* = 13 °C, *T_{deg}* = 242 °C. ¹H NMR (300 MHz, CDCl₃): δ 2.76-2.56 (m, 9H), 3.64 (dt, *J* = 18.6, 4.8 Hz, 4H), 4.01 (t, *J* = 2.5 Hz, 2H), 4.26 (t, *J* = 5.6 Hz, 4H), 7.02 (s, 1H). ¹H NMR (300 MHz, DMSO-d₆): δ 2.32 (t, *J* = 6.8 Hz, 2H), 2.57-2.48 (m, 6H), 3.02 (t, *J* = 2.3 Hz, 1H), 3.60-3.45 (m, 4H), 3.81 (dd, *J* = 5.4, 2.4 Hz, 2H), 4.11 (dt, *J* = 30.3, 5.3 Hz, 4H), 8.19 (t, *J* = 5.5 Hz, 1H).

TR-PPDAPE (TR4): Recovered = 572 mg, *M_n* = 26.0 kDa, *D_M* = 1.40, *T_g* = 22 °C, *T_{deg}* = 309 °C. ¹H NMR (300 MHz, CDCl₃): δ 1.63-1.51 (m, 6H), 2.62 (dd, *J* = 6.9, 6.3 Hz, 4H), 2.68 (s, 4H), 3.53-3.42 (m, 4H), 3.65 (dt, *J* = 28.0, 5.7 Hz, 4H), 4.29-4.20 (m, 4H).

TR-dnBuAPE (TR5): Recovered = 641 mg, *M_n* = 44.5 kDa, *D_M* = 1.42, *T_g* = -4 °C, *T_{deg}* = 315 °C. ¹H NMR (300 MHz, CDCl₃): δ 0.92 (dt, *J* = 12.8, 7.2 Hz, 6H), 1.36-1.24 (m, 4H), 1.60-1.45 (m, 4H), 2.65 (ddd, *J* = 13.6, 10.2, 5.8 Hz, 8H), 3.27 (q, *J* = 7.5 Hz, 4H), 3.71-3.58 (m, 4H), 4.27-4.19 (m, 4H).

TR-HepAPE (TR6): Recovered = 712 mg, *M_n* = 56.8 kDa, *D_M* = 1.34, *T_g* = 9 °C, *T_{deg}* = 277 °C. ¹H NMR (300 MHz, CDCl₃): δ 0.87 (q, *J* = 4.2 Hz, 3H), 1.27 (d, *J* = 3.3 Hz, 8H), 1.49-1.45 (m, 2H), 2.52-2.47 (m, 2H), 2.61 (d, *J* = 13.4 Hz, 4H), 2.74-2.70 (m, 2H), 3.22-3.16 (m, 2H), 3.68-3.58 (m, 4H), 4.26-4.20 (m, 4H), 6.35 (s, 1H).

TR-iPrAPE (TR7): Recovered = 1.82 g, *M_n* = 56.5 kDa, *D_M* = 1.57, *T_g* = 10 °C, *T_{deg}* = 287 °C. ¹H NMR (500 MHz, CDCl₃): 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-dEtAPE (TR8): Recovered = 519 mg, $M_n = 47.1$ kDa, $D_M = 1.66$, $T_g = -4$ °C, $T_{deg} = 304$ °C. ^1H NMR (500 MHz, CDCl_3): δ 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-PyrAPE (TR9): Recovered = 1.18 g, $M_n = 54.2$ kDa, $D_M = 1.60$, $T_g = 0$ °C, $T_{deg} = 307$ °C. ^1H NMR (500 MHz, CDCl_3): δ 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-THFAPE (TR10): Recovered = 187.4 mg, $M_n = 48.5$ kDa, $D_M = 1.49$, $T_g = 13$ °C, $T_{deg} = 275$ °C. ^1H NMR (500 MHz, CDCl_3): δ 1.54 (dt, $J = 18.6, 8.7$ Hz, 1H), 1.97-1.87 (m, 3H), 2.54 (t, $J = 6.4$ Hz, 2H), 2.65-2.60 (m, 4H), 2.72 (q, $J = 6.3$ Hz, 2H), 3.16 (dd, $J = 13.4, 6.0$ Hz, 1H), 3.53-3.48 (m, 1H), 3.61 (t, $J = 4.5$ Hz, 2H), 3.67 (t, $J = 5.7$ Hz, 2H), 3.73 (q, $J = 7.3$ Hz, 1H), 3.85 (q, $J = 7.4$ Hz, 1H), 3.95 (dd, $J = 7.0, 3.6$ Hz, 1H), 4.24 (dt, $J = 13.2, 6.2$ Hz, 4H), 6.49 (s, 1H).

TR-EoEtAPE (TR11): Recovered = 360 mg, $M_n = 30.3$ kDa, $D_M = 1.38$, $T_g = 9$ °C, $T_{deg} = 273$ °C. ^1H NMR (300 MHz, CDCl_3): δ 1.19 (t, $J = 7.0$ Hz, 3H), 2.53 (t, $J = 6.5$ Hz, 2H), 2.62 (d, $J = 14.4$ Hz, 5H), 2.71-2.69 (m, 2H), 3.40 (d, $J = 5.4$ Hz, 2H), 3.50-3.46 (m, 4H), 3.66 (t, $J = 5.7$ Hz, 4H), 4.23 (q, $J = 6.5$ Hz, 4H), 6.42 (s, 1H).

TR-MorAPE (TR12): Recovered = 486 mg, $M_n = 31.4$ kDa, $D_M = 1.35$, $T_g = 4$ °C, $T_{deg} = 306$ °C. ^1H NMR (300 MHz, CDCl_3): δ 2.66 (ddd, $J = 22.0, 9.6, 5.9$ Hz, 8H), 3.71-3.51 (m, 12H), 4.29-4.20 (m, 4H).

TR-bMoEtAPE (TR13): Recovered = 1.12 g, $M_n = 113.5$ kDa, $D_M = 1.58$, $T_g = -20$ °C, $T_{deg} = 315$ °C. ^1H NMR (300 MHz, CDCl_3): δ 2.66 (dq, $J = 20.0, 6.2$ Hz, 8H), 3.31 (d, $J = 7.0$ Hz, 6H), 3.70-3.47 (m, 12H), 4.22 (dt, $J = 13.5, 6.3$ Hz, 4H).

TR-MoEtAPE (TR14): Recovered = 153 mg, $M_n = 43.7$ kDa, $D_M = 1.39$, $T_g = -8$ °C, $T_{deg} = 266$ °C. ^1H NMR (500 MHz, CDCl_3): δ 1.18 (t, $J = 7.0$ Hz, 3H), 2.52 (t, $J = 6.5$ Hz, 2H), 2.64-2.59 (m, 4H), 2.71 (t, $J = 6.4$ Hz, 2H), 3.40 (q, $J = 5.3$ Hz, 2H), 3.51-3.46 (m, 4H), 3.59 (t, $J = 4.5$ Hz, 2H), 3.66 (t, $J = 5.7$ Hz, 2H), 4.23 (dt, $J = 12.7, 6.1$ Hz, 4H), 6.43 (dd, $J = 17.0, 5.4$ Hz, 1H).

TR-nPrPE (TR15): Recovered = 756 mg, $M_n = 25.3$ kDa, $D_M = 1.57$, $T_g = -20$ °C. ^1H NMR (300 MHz, CDCl_3): δ 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 δ 1.19 and δ 4.01

TR-iPrPE (TR16): Recovered = 396 mg, $M_n = 17.1$ kDa, $D_M = 1.37$, $T_g = -2$ °C. ^1H NMR (300 MHz, CDCl_3): δ 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 δ 1.19 and δ 4.01.

TR-MePE (TR18): Recovered = 484 mg, $M_n = 45.3$ kDa, $D_M = 1.3$, $T_g = -5$ °C. ^1H NMR (300 MHz, CDCl_3): δ 2.12 (s, 3H), 2.61 (t, $J = 3.8$ Hz, 4H), 3.60 (q, $J = 6.5$ Hz, 4H), 4.23 (t, $J = 5.4$ Hz, 4H).

TR-MoMePE (TR19): Recovered = 703 mg, $M_n = 23.1$ kDa, $D_M = 1.43$, $T_g = -9$ °C, $T_{deg} = 290$ °C. ^1H NMR (300 MHz, CDCl_3): δ 2.61 (s, 4H), 3.41 (s, 3H), 3.62 (t, $J = 5.6$ Hz, 4H), 4.14 (s, 2H), 4.25 (q, $J = 5.7$ Hz, 4H).

TR-MoEtPE (TR20): Recovered = 1.40 g, $M_n = 75.4$ kDa, $D_M = 1.47$, $T_g = -13$ °C, $T_{deg} = 294$ °C. ^1H NMR (300 MHz, CDCl_3): δ 2.61 (d, $J = 7.0$ Hz, 7H), 3.33 (s, 3H), 3.70-3.61 (m, 6H), 4.23 (d, $J = 3.4$ Hz, 4H).

II. NMR Spectra of Monomers and Polymers

