

## ELECTRONIC SUPPLEMENTARY INFORMATION

### SYNTHESIS AND CHARACTERIZATION OF MULTI-ARMED CALIXARENE- AND RESORCINARENE-CORE POLYLACTIDE STAR POLYMERS

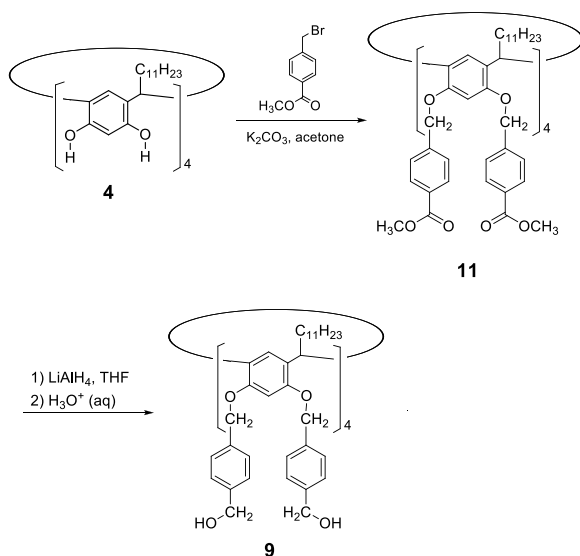
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#### I. Synthesis of Resorcinarene Initiator **9**:



**Materials and Methods.** All reactions were carried out under a dry nitrogen atmosphere unless indicated otherwise. Acetone was dried over 4 Å molecular sieves prior to use. Anhydrous THF (Aldrich) and all other solvent/reagents were used as received without further purification.

Resorcinarene **4** was prepared according to literature procedures.<sup>1</sup> Fourier-transform infrared (FTIR) spectra were acquired using a Perkin-Elmer Spectrum-One FTIR spectrophotometer equipped with a

universal ATR assembly. Ultraviolet-Visible (UV-Vis) spectra were acquired using either a Perkin-Elmer Lambda-2 or a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL ECS 400 NMR spectrometer ( $^1\text{H}$ , 400 MHz;  $^{13}\text{C}$ , 100 MHz).  $^1\text{H}$ -NMR chemical shifts were referenced to the signals arising from residual protio solvent in chloroform-*d* ( $\text{CDCl}_3$ ) and acetone-*d*<sub>6</sub>. Likewise,  $^{13}\text{C}$ -NMR spectra were referenced to solvent peaks. Coupling constants (*J*) in  $^1\text{H}$ -NMR spectra are given in Hertz, and broad signals are denoted by the abbreviation “br”. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were acquired using a Bruker MicroFlex R20 spectrometer. Elemental analyses were performed in the Microanalysis Laboratory of the School of Chemical Sciences at the University of Illinois at Urbana-Champaign.

**Resorcinarene 11.** C-undecylcalix[4]resorcinarene **4** (1.502 g, 1.36 mmol), methyl-4-(bromomethyl)benzoate (2.562 g, 11.15 mmol), and potassium carbonate (4.503 g, 32.6 mmol) were combined in a flame-dried, 250-mL round-bottomed flask equipped with reflux condenser and  $\text{CaSO}_4$  drying tube. Acetone was added to the flask, and the reaction mixture was heated at reflux for five days or until no starting material remained by TLC. The reaction mixture was cooled to room temperature, and the resulting slurry was filtered through a pad of celite. Acetone was subsequently removed by rotary evaporation to provide the crude product. The crude product was purified by column chromatography by first eluting excess methyl-4-bromobenzoate using a 20% (v/v) solution of ethyl acetate in hexanes as the mobile phase, followed by elution with a 50% (v/v) solution of ethyl acetate in hexanes. After combining fractions that contained the desired product ( $R_f = 0.44$ , 1:1 ethyl acetate/hexanes), solvent was removed by rotary evaporation, and the isolated product was further purified by recrystallization from methanol/dichloromethane. The resulting sample was dried *in vacuo* to provide 2.58 g (83%) of the desired product as a white solid: mp 150-152 °C;  $^1\text{H}$ -NMR (acetone-*d*<sub>6</sub>, 50 °C)  $\delta$  7.77 (br d, 4H, Ar-H), 7.29 (s, 4H, Ar-H), 6.86 (s, 2H, Ar-H), 5.10 (d,  $J = 11.9$ , 2H, OCHAr), 4.86 (br d, OCHAr), 4.81 (t,  $J = 6.9$ , ArCHAr), 3.86 (s, 6H,  $\text{OCH}_3$ ), 2.03 (m, ArCHCH<sub>2</sub>,

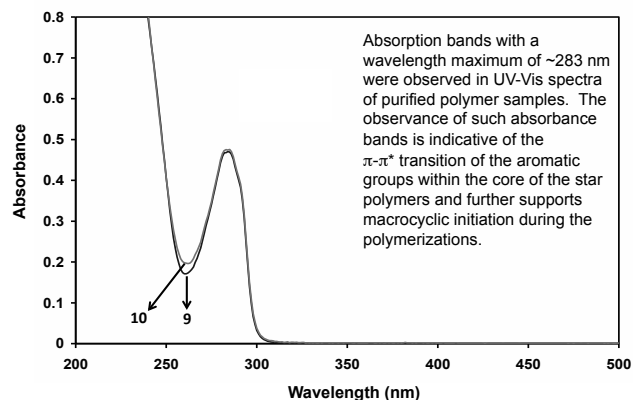
overlapped with protio solvent signal), 1.44 (m, CH<sub>2</sub>, 2H), 1.23-1.34 (br m, 16H, CH<sub>2</sub>), 0.85 (t,  $J = 6.8$ , 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>, 25 °C) δ 166.82, 155.95 (br), 143.69, 129.99, 127.49, 127.01, 99.39 (br), 70.37, 52.22, 37.94, 34.95, 32.62, 30.79, 30.64, 30.55, 30.51, 30.11, 23.31, 14.34; IR (ATR, cm<sup>-1</sup>) 2924 (CH), 2853 (CH), 1713 (C=O); MS (MALDI) 2312.9 [M + Na]<sup>+</sup>, 2328.9 [M + K]<sup>+</sup>; Anal Calcd for C<sub>144</sub>H<sub>176</sub>O<sub>24</sub>: C, 75.50; H, 7.74 Found: C, 75.40; H, 7.79.

**Resorcinarene 9.** Glassware was oven-dried overnight and then flame-dried under vacuum prior to use. To a 250-mL three-necked flask equipped with a reflux condenser/bubbler, a nitrogen inlet, and air-free syringe adapter was added 35 mL of anhydrous THF. Lithium aluminum hydride (0.332 g, 8.73 mmol) was carefully added to the THF under a strong flow of nitrogen. In a separate round-bottomed flask, ester **11** (2.000 g, 0.87 mmol), which had been dried in *vacuo* at 80 °C for one hour prior to use, was dissolved in anhydrous THF (~25 mL). The lithium aluminum hydride suspension was cooled in an ice-bath, and the THF solution of resorcinarene **11** was added dropwise to the cooled suspension. After complete addition, the reaction mixture was allowed to warm to room temperature, heated at reflux for five hours, and then stirred at room temperature overnight. Excess lithium aluminum hydride was, subsequently, quenched by cooling the reaction mixture in an ice bath, followed by dropwise addition of water (~11 mL). The resulting suspension was transferred to a round-bottomed flask using a small amount of THF, water, and chloroform. The THF and chloroform were removed by rotary evaporation to provide a solid suspension. An aqueous solution of 2 M HCl was added to the suspension followed by chloroform. The mixture was transferred to a separatory funnel, and the aqueous layer was separated. The organic layer was washed twice with water and then with a saturated aqueous solution of sodium chloride. The organic layer was dried over magnesium sulfate, and solvent was removed by rotary evaporation to give 1.76 g of crude product. The product was purified by recrystallization by heating the solid in hot (not boiling) diisopropyl ether (150 mL), followed by addition of 1.5 mL of boiling methanol. The product was precipitated by cooling to room temperature, collected by vacuum filtration, and dried *in vacuo* to give 1.08 g (60%) of the purified product as a white solid. mp 136-139

°C;  $^1\text{H-NMR}$  (acetone- $d_6$ , 50 °C)  $\delta$  7.18 (br s, 8H, Ar-H), 6.86 (br s, 1H, Ar-H), 6.75 (s, 1H, Ar-H), 4.93 (d,  $J = 11.4$ , Ar-CH), 4.78 (t,  $J = 6.2$ , ArCHAR), 4.74 (d,  $J = 11.4$ , ArCH), 4.58 (d,  $J = 5.5$ , 4H, ArCH<sub>2</sub>OH), 4.02 (t,  $J = 5.0$ , OH), 1.96 (m, 2H, CH<sub>2</sub>), 1.25-1.45 (m, 18H, CH<sub>2</sub>), 0.86 (t,  $J = 6.9$ , 3H, CH<sub>3</sub>);  $^{13}\text{C NMR}$  (acetone- $d_6$ , 25 °C)  $\delta$  155.49 (br), 141.66, 136.68, 127.39, 126.55, 126.20, 99.27 (br), 70.36, 63.92, 63.79, 36.64, 34.68, 32.06, 30.29, 30.08, 30.01, 29.94, 29.84, 29.54, 28.93, 22.74, 13.78; IR (ATR,  $\text{cm}^{-1}$ ) 3310 (OH), 2921 (C-H), 2852 (C-H); MS (MALDI) 2088.8  $[\text{M} + \text{Na}]^+$ , 2104.7  $[\text{M} + \text{K}]^+$ ; Anal Calcd for C<sub>136</sub>H<sub>176</sub>O<sub>16</sub>: C, 79.03; H, 8.58. Found: C, 78.74; H, 8.41.

## II. Representative UV-Vis Spectral Data:

In addition to the evidence presented within the manuscript text, UV-Vis spectral analysis was also carried out with selected polymers to further verify incorporation of the macrocyclic core within the star polymers. A representative spectrum is shown in Fig. S11.



**Figure S11.** UV-Vis spectra of  $2.15 \times 10^{-5}$  M solutions of resorcinarene initiator **9** and URBEN-DLPLA<sub>8</sub>, **10** ( $M_n$  GPC = 13.4 kDa) in acetonitrile.

### IIIA. Mass Peak List and Calculated Masses for the MALDI Mass Spectrum in Figure 6A.

Measured $m/z^a$	Calculated $m/z^a$	Overall DP
2794.2	2793.7	27
2865.5	2865.8	28
2940.6	2937.9	29
3009.6	3009.9	30
3082.4	3082.0	31
3154.0	3154.0	32
3225.4	3226.1	33
3297.9	3298.2	34
3370.8	3370.2	35
3442.0	3442.3	36
3514.3	3514.3	37
3586.2	3586.4	38
3658.9	3658.5	39
3730.3	3730.5	40
3802.1	3802.6	41
3874.6	3874.6	42
3946.7	3946.7	43
4018.7	4018.8	44
4090.7	4090.8	45
4163.3	4162.9	46
4235.0	4234.9	47
4307.0	4307.0	48
4379.1	4379.1	49
4451.3	4451.1	50
4522.9	4523.2	51
4595.5	4595.2	52
4667.6	4667.3	53
4739.7	4739.4	54
4811.7	4811.4	55
4883.8	4883.5	56
4955.4	4955.5	57
5028.2	5027.6	58
5099.9	5099.7	59
5172.3	5171.7	60
5243.7	5243.8	61
5316.0	5315.8	62
5388.0	5387.9	63
5460.2	5460.0	64
5532.7	5532.0	65
5604.6	5604.1	66
5676.6	5676.1	67
5748.9	5748.2	68
5821.3	5820.3	69
5892.8	5892.3	70
5964.5	5964.4	71
6036.5	6036.4	72
6109.0	6108.5	73
6180.8	6180.6	74
6252.9	6252.6	75
6325.2	6324.7	76
6397.7	6396.7	77
6469.8	6468.8	78
6542.5	6540.9	79
6613.4	6612.9	80
6685.6	6685.0	81
6756.9	6757.0	82
6829.4	6829.1	83
6901.8	6901.2	84
6973.5	6973.2	85
7046.1	7045.3	86
7119.4	7117.3	87
7191.0	7189.4	88
7262.0	7261.5	89
7336.6	7333.5	90

<sup>a</sup>[M + Na]<sup>+</sup>

### IIIB. Mass Peak List and Calculated Masses for the MALDI Mass Spectrum in Figure 6B.

Measured $m/z^a$	Calculated $m/z^a$	Total DP
6959.5	6959.7	76
7032.1	7031.7	77
7104.5	7103.8	78
7177.2	7175.8	79
7248.9	7247.9	80
7319.7	7320.0	81
7392.5	7392.0	82
7465.0	7464.1	83
7536.7	7536.1	84
7609.1	7608.2	85
7680.9	7680.3	86
7752.8	7752.3	87
7824.5	7824.4	88
7897.4	7896.4	89
7970.6	7968.5	90
8041.1	8040.6	91
8113.6	8112.6	92
8185.4	8184.7	93
8257.2	8256.7	94
8329.3	8328.8	95
8402.9	8400.9	96
8475.0	8472.9	97
8547.2	8545.0	98
8618.0	8617.0	99
8689.9	8689.1	100
8762.5	8761.2	101
8834.6	8833.2	102
8906.7	8905.3	103
8979.4	8977.3	104
9051.1	9049.4	105
9122.7	9121.5	106
9195.2	9193.5	107
9267.7	9265.6	108
9339.5	9337.6	109
9412.4	9409.7	110
9483.7	9481.8	111
9555.0	9553.8	112
9627.9	9625.9	113
9700.0	9697.9	114
9772.1	9770.0	115
9844.3	9842.1	116
9915.9	9914.1	117
9988.7	9986.2	118
10060.2	10058.2	119
10132.6	10130.3	120
10205.0	10202.4	121
10277.0	10274.4	122
10349.2	10346.5	123
10420.8	10418.5	124
10493.2	10490.6	125
10565.0	10562.7	126
10637.4	10634.7	127
10709.2	10706.8	128
10781.3	10778.8	129
10853.3	10850.9	130
10925.8	10923.0	131
10998.3	10995.0	132
11070.4	11067.1	133
11142.4	11139.1	134
11213.6	11211.2	135
11286.3	11283.3	136
11358.4	11355.3	137
11431.2	11427.4	138
11502.1	11499.4	139
11575.1	11571.5	140

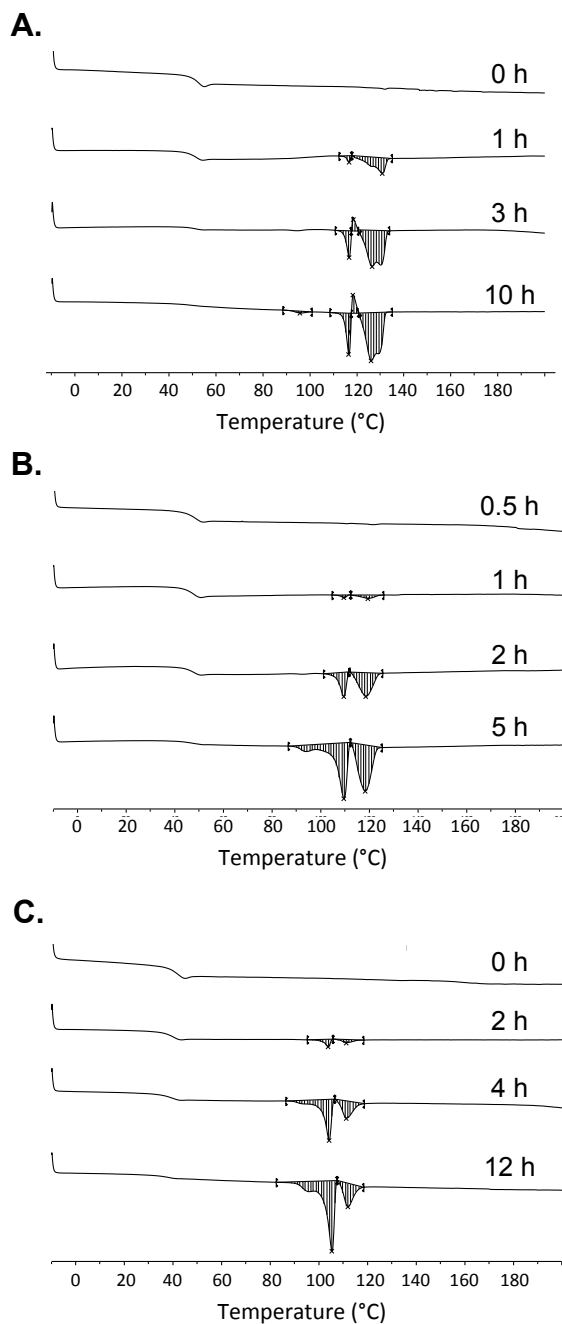
<sup>a</sup>[M + Na]<sup>+</sup>

Measured $m/z^a$	Calculated $m/z^a$	Total DP
11646.9	11643.6	141
11718.0	11715.6	142
11792.5	11787.7	143
11862.7	11859.7	144
11936.8	11931.8	145
12008.3	12003.9	146
12079.2	12075.9	147
12152.8	12148.0	148
12224.1	12220.0	149
12295.8	12292.1	150
12368.5	12364.2	151
12440.2	12436.2	152
12512.6	12508.3	153
12585.8	12580.3	154
12656.5	12652.4	155
12728.5	12724.5	156
12799.9	12796.5	157
12872.8	12868.6	158
12946.5	12940.6	159
13017.6	13012.7	160
13086.7	13084.8	161
13162.0	13156.8	162
13228.5	13228.9	163
13306.2	13300.9	164
13373.9	13373.0	165
13450.5	13445.1	166
13522.0	13517.1	167
13594.5	13589.2	168
13665.0	13661.2	169
13742.8	13733.3	170
11646.9	11643.6	141
11718.0	11715.6	142
11792.5	11787.7	143
11862.7	11859.7	144
11936.8	11931.8	145
12008.3	12003.9	146
12079.2	12075.9	147
12152.8	12148.0	148
12224.1	12220.0	149
12295.8	12292.1	150
12368.5	12364.2	151
12440.2	12436.2	152
12512.6	12508.3	153
12585.8	12580.3	154
12656.5	12652.4	155
12728.5	12724.5	156
12799.9	12796.5	157
12872.8	12868.6	158
12946.5	12940.6	159
13017.6	13012.7	160
13086.7	13084.8	161
13162.0	13156.8	162
13228.5	13228.9	163
13306.2	13300.9	164
13373.9	13373.0	165
13450.5	13445.1	166
13522.0	13517.1	167
13594.5	13589.2	168
13665.0	13661.2	169

<sup>a</sup>[M + Na]<sup>+</sup>

#### IV. Differential Scanning Calorimetry Data

Representative DSC data was provided within the text for a UR-LPLA<sub>6</sub> star polymer, **6**. Sample DSC data arising from annealing studies with a CALIX-LPLA<sub>4</sub> (**3**), OBRA-LPLA<sub>4</sub> (**8**), and URBEN-LPLA<sub>6</sub> (**10**) is provided in Fig. SI2. Annealing studies were carried out by pre-melting the LPLAs within a DSC pan at 165 °C (heated for 15 min.). The samples were then cooled to 85 °C at a rate of 25 °C/min and held at this temperature for times varying between 0.5 and 24 h. The LPLAs were then cooled to -10 °C (rate = 20 °C/min), equilibrated for 15 min., and heated to 200 °C at a rate of 5 °C/min. The DSC traces for unannealed samples (0 h annealing) shown in Figure SI2 were obtained from the second heating cycle of a standard DSC run (heating/cooling rate = 5 °C/min; temperature range = -10 °C to 200 °C). As illustrated in Fig. SI2A, the samples annealed for 3 and 10 h appear to have two melting endotherms separated by a crystallization exotherm. Similar results were observed for unannealed samples of **3** with higher  $M_n$ .



**Figure SI2.** a) DSC traces for a CALIX-LPLA<sub>4</sub>, **3** ( $M_n$  NMR = 8.6 kDa; DP/arm NMR = 27) that was annealed for varied amounts of time. b) DSC traces for an OBRA-LPLA<sub>4</sub>, **8** ( $M_n$  NMR = 8.4 kDa; DP/arm NMR = 24) that was annealed for varied amounts of time. c) DSC traces for an URBEN-LPLA<sub>8</sub>, **10** ( $M_n$  NMR = 13.3 kDa; DP/arm NMR = 20) that was annealed for varied amounts of time.

## REFERENCES

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