Supplementary Material

Spatially Directional Multiarm Poly(ε-Caprolactone) Based on Resorcin[4]arene Cavitand Core

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Table of contents

General methods……..2
Synthesis of Octol- resorcin[4]arene (1)……..…2
Synthesis of bridged resorcin[4]arene (2a)……...…3
Synthesis of tetrabromide cavitand (2b)…….…….3
Synthesis of Tetrol cavitand (2c)……..…3
General procedure of synthesis of directional poly(ε-caprolactone)…….…...3
Figure S1- DSC thermograms……..……...4
Figure S2- Representitive GPC chromatogram…….5
Figure S3- Dept 135-NMR (125 MHz, $CDCl_3$) spectrum of $2cSPL_{40}$……..…6
References……..…..…6

General methods:

Materials: All reagents were used without further purification unless otherwise are specified. Stannous 2-ethyl-hexanoate (stannous octanoate, 95%) was purchased from the Aldrich Chemical Company. ε-Caprolactone was dried over CaH_2 and distilled under reduced pressure and stored under nitrogen atmosphere. Azobisisobutylonitrile (AIBN) was crystallized from hot ethanol. N-bromosuccinimide (NBS) was crystallized prior use from boiling water.

Measurements. Molecular weights were measured by gel permeation chromatography (GPC) using a Shimadzu HPLC system equipped with a model LC-10ADvp pump, model SIL-10A auto injector, model RID-10A refractive index detector (RI), model SPD-10AV UV-Vis detector, and waters HR 4E styragel column. $CHCl_3$ (HPLC grade) was used as an eluent at a flow rate of 1.0 mL/min. The sample concentration and injection volumes were 0.5 % (w/v) and 100 µL, respectively. EzChrome Elite (Scientific Software Inc.) was used to calculate molecular weights based on a calibration curve generated by narrow molecular weight distribution polystyrene standards (5.00×10^2, 8.00×10^2, 2.10×10^3, 4.00×10^3, 9.00×10^3, 1.90×10^4, 5.00×10^4, 9.26×10^4, 2.33×10^5, and 3.00×10^5 g/mol, Perkin-Elmer).

NMR analysis: ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker DPX-250, and Varian Inova 500 spectrometers. Sample concentrations were about 10% (w/v) in $CDCl_3$ containing 1% TMS as an internal reference.

Thermal analysis: Thermal analyses were preformed on a Dupont DSC 2920 TA instrument attached to a Thermal Analyst 2000 TA instrument computer. Indium was used as the standard for the temperature calibration and the analyses were made under constant stream of nitrogen with a heating rate 10 ^{o}C/min and cooling rate of 40 ^{o}C/min. The relative crystallinity of samples was calculated according to equation 1:

$$X_c = \frac{\Delta H_m}{\Delta H_m^*} \times 100 \qquad (1)$$

Where *Xc* is the percent crystallinity, ΔH_m is the enthalpy of melting of the sample, and ΔH_m^o is the heat of melting of 100% crystalline PCL. The value of ΔH_m^o used in the calculation is 136.4 J/g.[1]

Thermogravimetric analysis (TGA) measurements were performed with a PerkinElmer STA 6000 Simultaneous Thermal Analyzer (purge gas nitrogen and scan rate of 10^{o}C/Min). The decomposition temperatures (Td) of the polymers were measured at 10% weight lost.

Wide-angle X-ray scattering (WAXS): WAXS spectra were collected with a Bruker AXS D8 Advance powder diffractometer with CuK α radiation (λ = 1.54058Å A°). Samples were analyzed from 3^o to 40^o 2θ using a step size of 0.05^o 2θ with a collection time of 0.5 per step at 25 ^{o}C.

Synthesis of Octol-resorcin[4]arene (1):[2]

Methyl resorcinol (10g, 0.081mol) was dissolved in ethanol (62.7mL, 775mL/mol) and 37% aqueous HCl (15.1mL, 185mL/mol). The solution was cooled in ice bath and heptaldehyde

(11.3mL, 0.081mol) was added slowly over a period of 30 min. The reaction mixture was allowed to warm to room temperature and refluxed for 12 h. The yellow colored precipitate was filtered and washed several times with distilled water until it turns neutral to pH paper. Yield 10.7g (**88** %). MP: >220 ^{o}C(decomposed). ^{1}H NMR (250 MHz, DMSO-d6) δ: 0.84 (t, 12H, J = 6.25Hz), 1.23(m, 32H), 1.93(s, 12H), 2.21(s, 8H), 4.18 (t, 4H J = 7.75Hz)), 7.21 (s, 4H), 8.69(bs, 8H). 13C NMR (100 MHz, DMSO-d6) δ: 10.7, 14.2, 22.9, 28.9, 29.8, 32.1, 35.4, 38.4, 73.0, 113.6, 122.0, 124.6, 154.0.

Synthesis of bridged resorcin[4]arene (2a):[3]

Compound **1** (5g, 5.5 mmol) was dissolved in 55 mL DMF in 125 mL in sure-sealed tube. Potassium carbonate (12 g, 88 mmol) was added and stirred for 0.5 h. Then bromochloromethane (7.7 mL, 88 mmol) was added at room temperature. The reaction mixture was sealed and immersed in preheated oil bath 80 ^{o}C for 24h. The reaction mixture was poured into cold ice water and the white solid was collected by section filtration. Yield 4.9 g (**94** %). ^{1}H NMR (250 MHz, $CDCl_3$) δ: 0.82 (t, 12H, J = 6.25Hz), 1.23(m, 32H), 1.90 (s, 12H), 2.11(s, 8H), 4.17 (d, 4H J = 7.0), 4.69 (t, 4H J = 8.0 Hz), 5.79 (d, 4H J = 7.0), 6.90 (s, 4H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 10.3, 14.1, 22.7, 27.9, 29.2, 30.1, 31.8, 37.0, 98.5, 117.6, 123.6, 137.9 153.2.

Synthesis of tetrabromide cavitand (2b):[4]

Compound **2a** (4g, 4.3 mmol) and AIBN (100, 0.6 mmol) dissolved in 50 mL degassed benzene. Then NBS (5.4g, 30 mmol) was added and the reaction mixture was reflux overnight. After completion the solid precipitate (succinimide) was filtered off and benzene was evaporated. The residue was dissolved in acetone and crystallized by the addition of ethanol. White precipitate was collected. Yield 4.4g (**83** %). MP: >104 ^{o}C(sublime). ^{1}H NMR (250 MHz, $CDCl_3$) δ: 0.82 (t, 12H, J = 6.25Hz)), 1.22(m, 32H), 2.12 (m, 8H), 4.34 (s, 8H), 4.46 (d, 4H J = 7.0), 4.71 (t, 4H J = 7.75 Hz), 5.94 (d, 4H J = 7.75), 7.06 (s, 4H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ:, 14.1, 22.6, 23.0, 27.3, 29.5, 30.1, 36.8, 99.1, 121.0, 124.5, 138.1, 153.5.

Synthesis of Tetrol cavitand (2c):[4]

Compound **2b** (1g, 0.8 mmol) was dissolved in 40 acetone/water (9:1) in sure-sealed tube. Then K_2CO_3 (0.3g, 2.2 mmol) was added, and the reaction mixture was immersed in preheated oil bath at 80 ^{o}C for 24h. After completion the acetone was evaporated and residue was dissolved in ethyl acetate and extracted with brine solution. The white solid was obtained as white solid after purification by plug silica gel eluting 20 % ethyl acetate/hexane. Yield 720 mg (**90** %). ^{1}H NMR (250 MHz, $CDCl_3$) δ: 0.81(t, 12H, CH_3), 1.21 (m, 32H), 2.23 (m, 8H,), 4.44 (m, 16H), 4.84 (t, 4H, J=7.32 Hz), 5.78 (d, 4H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 14.1, 22.6, 26.5, 27.8, 29.4, 30.1, 31.8, 36.8, 56.9, 100.2, 120.6, 137.9, 153.6.

General procedure of synthesis of directional poly(ε-caprolactone):

Dry resorcin[4]arene initiator (**2c**) was added into a 15 mL tube and dry under vacuum at 50^{o}C. Then the tube was cap by rubber ring under nitrogen atmosphere and ε-caprolactone was injected into the tube and warmed until the initiator dissolved. The tube was immersed in preheated oil bath at 120^{o}C and the catalyst (dry toluene solution, 1:200 catalyst/initiator ratios) was injected into reaction mixture immediately. The reaction was reacted for 24 hours to 48 hours and the product was dissolve in dichloromethane and precipitated in ice-cold methanol.

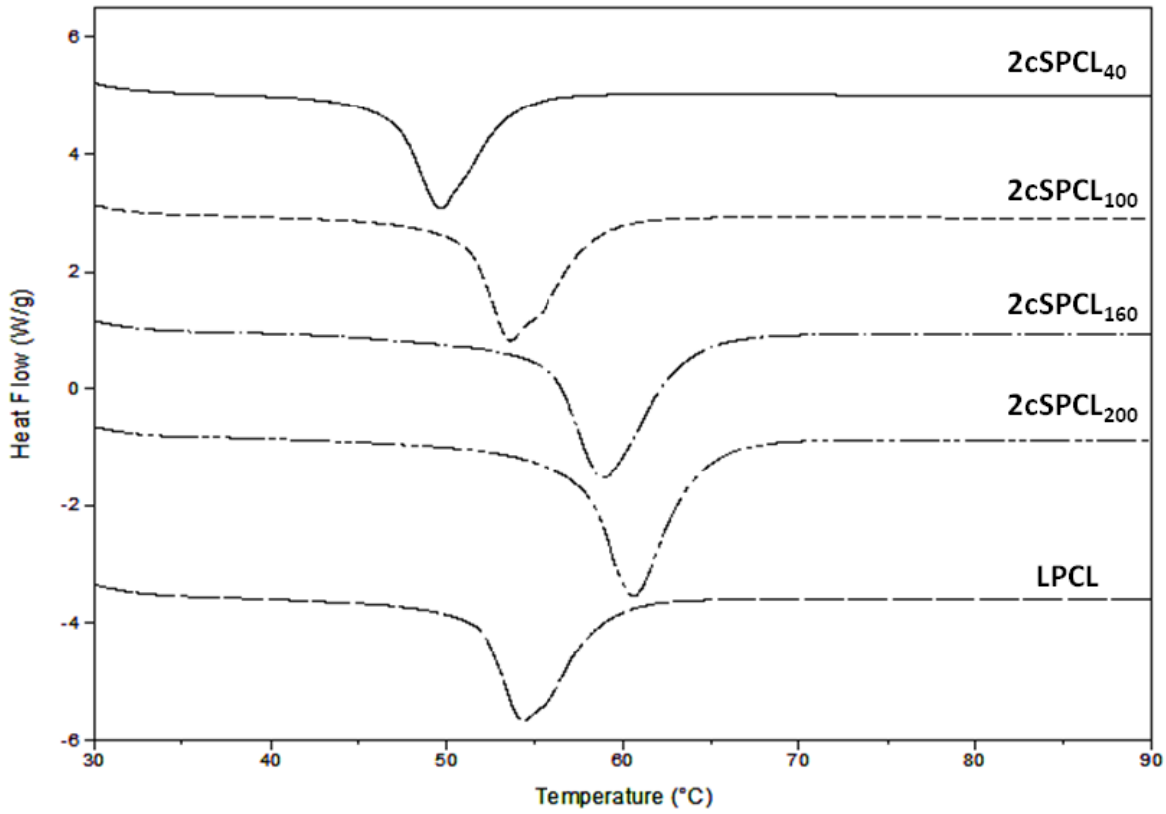

Figure S1. DSC thermograms of directional poly(ε-caprolactone)s (SPCL) and Linear Poly(ε-caprolactone) (LPCL).

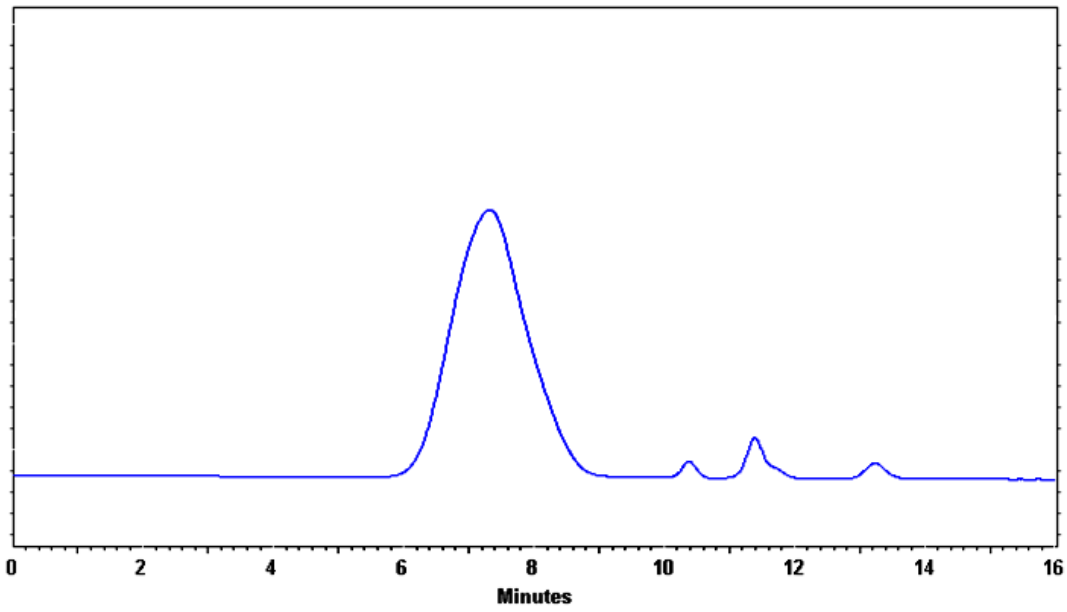

Figure S2. Representative GPC chromatogram of directional poly(ε-caprolctone), 2cSPCL$_{200}$ [Table 1, entry 4].

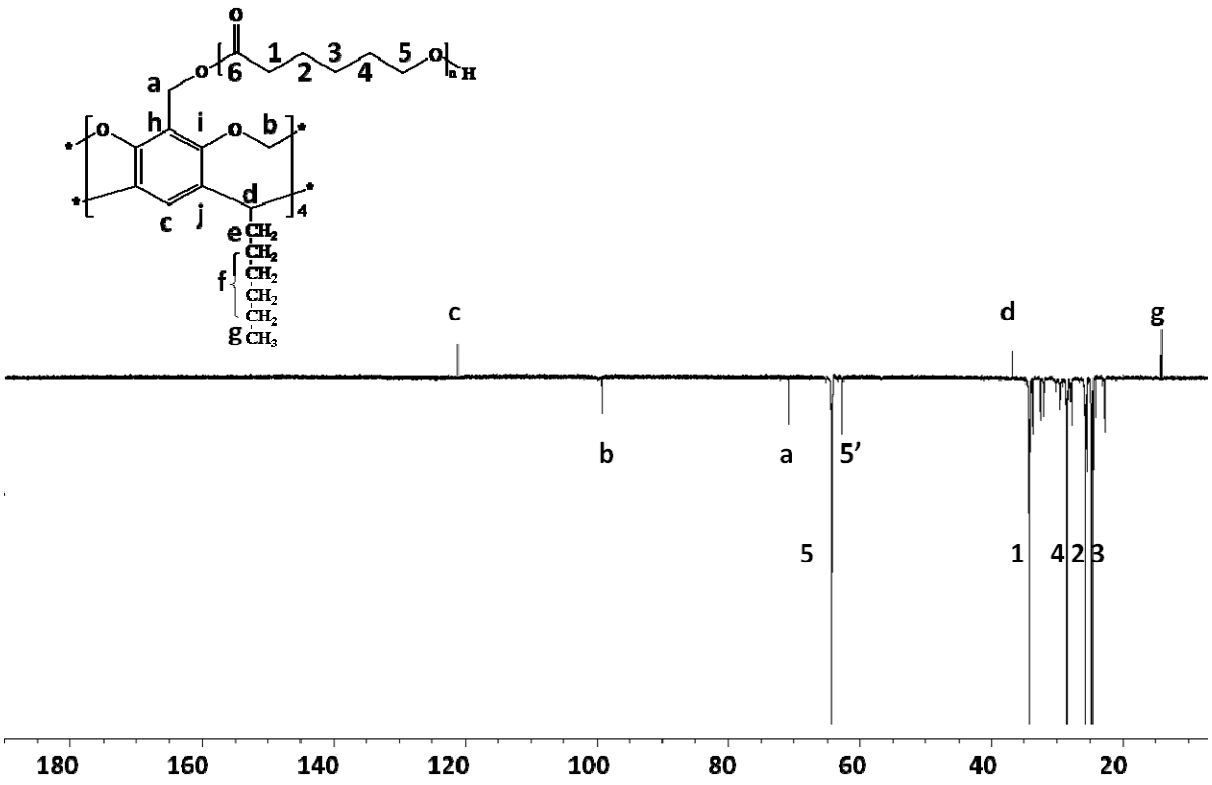

Figure S3. Dept135-NMR (125 MHz, $CDCl_3$) spectrum of $2cSPL_{40}$ [Table 1, entry 1] catalyzed by $Sn(Oct)_2$ at 120 ^oC.

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