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ARTICLE

Influence of Resorcin[4]arenes Core Structure on the Spatial Directionality of Multi-arm Poly(ε-caprolactone)s

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Highly crystalline directional polycarpolactones (PCL) based on two tetrahydroxymethyl resorcin[4]arenes initiators were synthesized by "core first" method via ring-opening polymerization of ε-caprolactone catalyzed by $Sn(Oct)_2$ in bulk at 120 ^oC. The synthesized polymers were characterized by NMR, TGA, DSC, and WAXS. The structure of tetra-arms PCLs based on resorcinarenes was confirmed by ^{1}HNMR analysis. The thermal properties were evaluated using DSC and TGA. The spatial directionality, a consequence of the rigid bowl shaped resorcinarene cavitand core, of the PCL chains influenced the thermal properties and crystallinity of the polymers. The T_m, T_d and %Xc of the directional PCL from the rigid core cavitand **2c** was significantly higher than that of the linear counterpart and the somewhat flexible cavitand core **3c**. The data implies that the spatial directionality of the polymer chains in multi-arm polymers can be used to manipulate their thermal and physical properties. Detailed analysis of the two tetra-hydroxy resorcinarenes initiators and the comparison with linear PCL is discussed.

Introduction

Linear aliphatic polyesters are of interest due to their biodegradability, biocompatibility, and permeability for many drugs.[1] This class of polymers have found their way in many biomedical applications such as surgical sutures, drug delivery systems, and internal bone fixation. Polycaprolactone (PCL), in particular, is an important biodegradable polymer and has been used as a long range drug release delivery system due it is slow rate of degradation.[1] In the last two decades, branched polymers such as star-polymers,[2] dendrimers,[3] and hyperbrached polymers[4] have attracted much attention for their unique architectures and wide range of potential applications in micelle formation, encapsulation, self-assembly, liquid crystal formation, thin films, electroluminescent devices, sensors, conductive and ionic conductive polymers, photochemical molecular devices, catalysts, and in biochemicals and pharmachemicals.

Multi-arm polymers have unusual bulk and solution properties, such as low melt viscosities compared to their linear counterparts, which can be molded at lower temperature especially for polymers with low thermal stability such as polyesters.[5] The synthesis of multi-arm polymers have essentially been via two main approaches, i.e., arms[6] and core[7] first methods; the latter involves the use of multifunctional core as initiator. The initiator core is used mainly to support the polymers arm with no further application for its presence and multi-arm polcaprolactone, polylatide, and poly(trimethylene carbonate) have synthesized using multifunctional alcohols.[4(c-f)]

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Attempts to utilize a different core have led to the use of multifunctional macrocylic compounds as initiators, for instance cyclodextrins,[8] calixarenes, and resorcinarenes[9-12] have all been used. Calixarenes and resorcinarenes are macrocylic phenolic compounds which have many potential applications as sensor materials for recognition of metal ions encapsulation, stabilization of guest molecules, and as catalyst platforms. Due to their simple preparation, unique structure and applications, star-shaped polymers have been synthesized based on calixerene and resorcinarenes as the initiator core and various polymerization techniques have been employed in the synthesis, e.g., atom transfer radical polymerization (ATRP),[9] reversible radical fragment transfer polymerization (RAFT),[10] living cationic polymerization,[11] and ring-opening polymerization (ROP).[12] However, there are only a few reports in the literature of multiarm-polymers based on resorcinarenes core synthesized by ROP.[13] Recently, we reported the first ever synthesis of a spatially directional polycaprolactone initiated by conformationally locked tetrahydroxy resorcinarene core via ring opening polymerization (ROP) catalyzed by tin octanoate $[Sn(Oct)_2]$.[13c]

In this work, we report the synthesis of tetra-arm polycaprolactone based on conformationally locked and unlocked resorcinarenes cores via ROP catalyzed by tin ocatanoate $Sn(Oct)_2$. Series of multi-arm polymers with different length arms were synthesized and were characterized by NMR spectroscopy, and gel permeation chromatography (GPC). Thermal properties were examined using differential scanning calorimetry (DSC), and thermogravimetric (TGA). Wide-angle X-ray scattering (WAXS) and DSC were used to evaluated the crystallinity of the polymers.

Results and Discussion

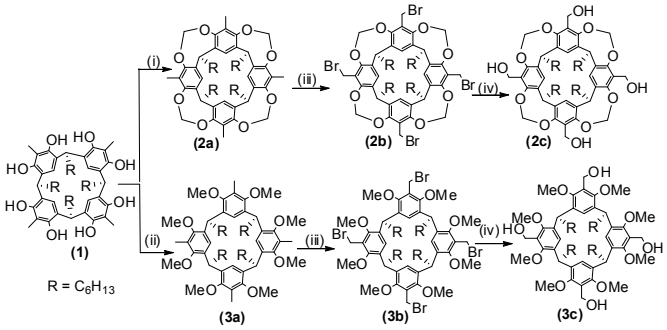
Table 1. Polymerization[#] of ε-CL with of resorcin[4]arene **2c** and **3**c

Entry	Polymer	M/I[a] (mol/mol)	Yield[b] (%)	Mn[c] (g/mol)	Mw/Mn[c]	Tm[d] (°C)	ΔH_m[d] (J/g)	T_d[e] (°C)	X_c[f] (%)
1	$2cSPL_{40}$	40	95	7000	2.2	49.7	55.6	351	41
2	$2cSPL_{100}$	100	93	8800	2.1	53.6	69.9	359	51
3	$2cSPL_{160}$	160	92	12000	2.0	58.9	88.9	363	65
4	$2cSPL_{200}$	200	93	15000	2.0	60.6	91.2	368	67
5	$3cSPL_{40}$	40	94	6500	2.0	49.5	52.4	350	38
6	$3cSPL_{100}$	100	92	7900	2.0	52.7	66.2	357	48
7	$3cSPL_{160}$	160	92	11500	1.9	54.3	70.2	361	51
8	$3cSPL_{200}$	200	91	14500	1.9	56.5	75.6	366	55
9	LPCL[g]	200	95	15400	1.5	54.3	65.1	349	48

[#]Polymerization condition; 120 °C for 24h in bulk. Initiator/catalyst (I/C) =200. [a]Monomer/initiator (M/I) = mole/mole. [b]Insoluble methanol portion. [c]Determined by GPC. [d]Measured by DSC. [e]Decomposition temperature measured by TGA at 10% decomposition. [f]Percent crystallinity (*X*c) measured from DSC.[7] [g]Linear polycaprolactone.

Synthesis of tetrol resorcin[4]arenes initiator cores

Tetrahydroxy methyl resorcinarenes initiators **2c** and **3c** were synthesized in three steps (Scheme 1). Compound (**1**) was synthesized by acid catalyzed condensation of 2-methyl resorcinol and heptanal. The conformationally locked (**2a**) was synthesized by reacting **1** with $ClCH_2Br$; whereas the synthesis of the unlocked compound (**2b**) was achieved by the reaction of octa-hydroxy (**1**) with methyl iodide. Bromination of the benzylic hydrogens with NBS yielded tetrabromo resorcinarenes (**2b** and **3b**), which were converted to the corresponding tetraol resorcinarenes (**2c** and **3c**) by treatment with water/acetone mixture in presence of K_2CO_3.



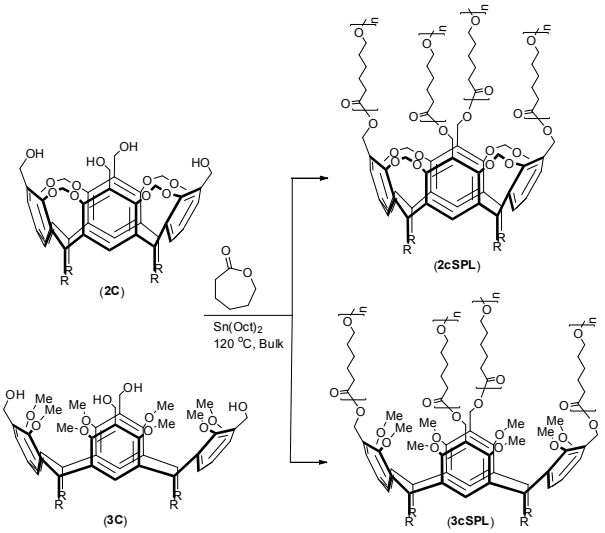
Scheme 1. Synthesis of tetrahydroxy resorcinarenes initiator cores: (i) $BrCH_2Cl$, K_2CO_3, DMF, 70 °C. (ii) CH_3I, K_2CO_3, Acetone. (iii) NBS, AIBN, benzene. (iv) H_2O/Acetone, K_2CO_3.

The R groups in the lower rim of the resorcinarene derivatives highly influence its solubility and conformation in solution. Shen *el at*[13a] have reported that the synthesis star-polycaprolactone based on resorcinarenes with methyl or phenyl groups on the lower rim failed due to their poor solubilities, however, when long alkyl chain the polymerization were successful. The C_6H_{13} hydrocarbon chain in the lower rim renders compounds **2c** and **3c** soluble in ε-caprolactone and reaction can be carried out in bulk. The homogeneity of the reaction mixture facilitates the synthesis of the multi-arm polycaprolactone.

Synthesis and Characterization of Tetra-Arm Poly(ε-caprolactone)s

Tetra-arm polycaprolactones from the resorcinarene caviutand core **2c** and **3c** were synthesized via ROP catalysed by Sn(Oct)2 at 120 °C in bulk for 24 hours (Scheme 2).

Table 1 summarizes the results obtained for the ROP of ε-caprolactone with **2c** and **3c** initiators catalyzed by Sn(Oct)2 at 120 °C in bulk for 24h. Four different length arms for two series based on initiator **2c** and **3c** were synthesized. The polymers where obtained in high yield (91-95%), and GPC analysis showed unimodel distributions for all set of series (Figure 1). The number-average molecular weight (Mn) for both sets of multi-arm polycaprolatone obtained from initiators **2c** and **3c** were comparable to each other and the polydispersities (PDI) ranged between 1.9 and 2.2.



Scheme 2. Synthesis of directional polycarpolactone based on resorcin[4]arenes **2c** and **3c**.

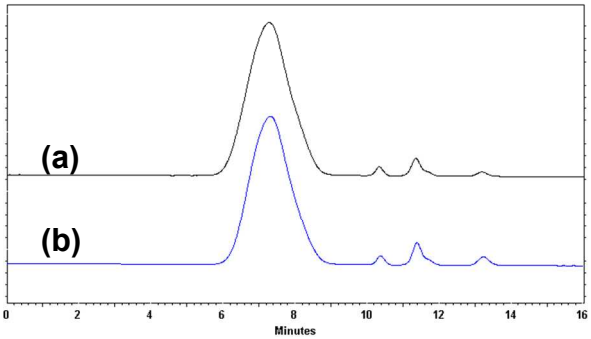


Figure 1. Representative GPC chromatograms: (a) $2cSPL_{200}$ [Table 1, entry 4]. (b) $3cSPL_{200}$ [Table 1, entry 8].

^{1}H-NMR spectra of $2cSPCL_{40}$ and $3cSPCL_{40}$, [Table 1, entry 1], and [Table 1, entry 5] are shown in Figure 2 and 3 respectively. The

spectral assignment is based on comparison with ^{1}H-NMR spectra of PCL and the resorcinarene initiators. In Figure 2, the high intensity resonances are assigned to the PCL repeating units, and low intensities resonances are characteristic of the initiator core **2c**. The peaks at 0.9 and 1.2 ppm are assigned to the methyl hydrogens (H_g, -C$\underline{H}_3$), and methylene hydrogens (H_f, C$\underline{H}_2$-) of the lower rim of the core. The methylene hydrogens H_e which appear around 2.2 ppm are buried under the PCL repeating units. A triplet at 3.6 ppm is characteristic of the methylene hydroxy end groups of PCL chains. The ratio of the end group methylene hydrogen integral to that of the CL repeating units (H5) were used to calculate the DP (13 for 2cSPL$_{40}$) and the molecular weight of the polymers were in very good agreement with the GPC measurements. The bridged methylene hydrogens (H_b) show at 4.75 and 5.75 ppm due to anisotropy of the resorcinarene cavity, i.e., the hydrogen on the inside of the cavity is shielded (4.75 ppm) compared to the one on the outside (5.75 ppm). Resonance at 4.70 ppm is for the hydrogen H_d and phenyl hydrogen H_c appeared at 7.15 ppm. The peak around 5.0 ppm is assigned to the methylene hydrogens (Ha, -C$\underline{H}_2$-O-CL) which indicate direct link between the PCL arms and the resorcinaerene initiator core **2c**. Importantly, the resonance position of the methyleneoxy hydrogen H_a is close to what has been reported previously in tetra-acetyl resorcinarene.[17] The area under the peaks of the methylene hydroxy end-groups at 3.52 (8H) and the hydrogen of the bridge at 5.75 (4H) are within the ratio of 0.5 which suggest that all the hydroxy groups are linked the PCL [see Figure 2].

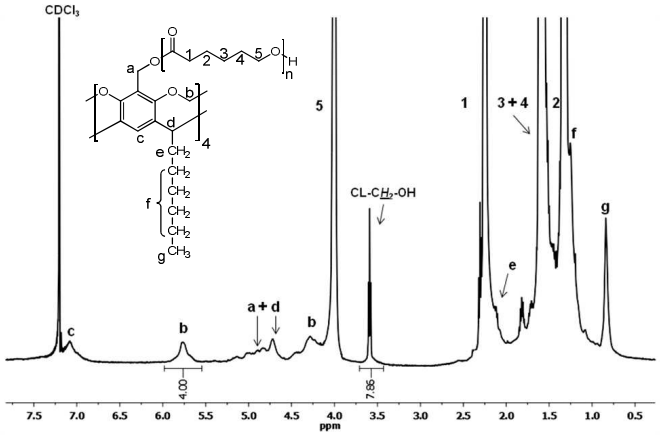


Figure 2. ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 2cSPL$_{40}$ [Table 1, entry 1] catalyzed by Sn(Oct)$_2$ at 120 ^{o}C.

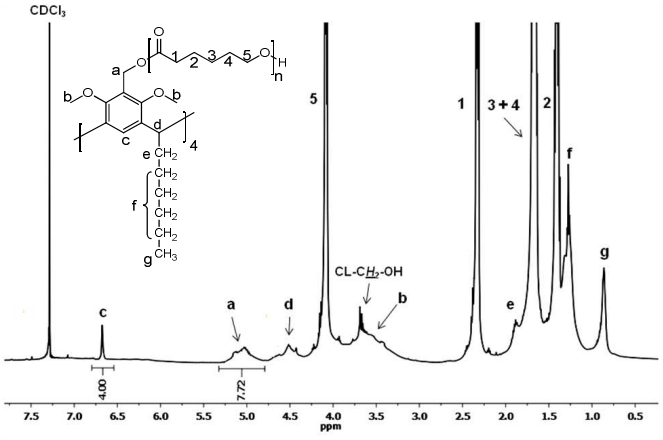


Figure 3. ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3cSPL$_{40}$ [Table 1, entry 5] catalyzed by Sn(Oct)$_2$ at 120 ^{o}C.

Figure 3 shows ^{1}HNMR spectrum of 3cSPCL$_{40}$ [Table 1, entry 5]. Along with the high intensity resonances for PCL repeating units, low intensity resonances are visible in the ^{1}HNMR spectrum corresponding to the resorcinarene imitator **3c**. The lower rim hydrogens are clearly apparent in the spectrum; the hydrogens H_g,H_f and H_d) appeared at 0.77, 1.19 and 1.79 ppm respectively. The methoxy hydrogens (H_b) on the upper rim appeared at 4.1 ppm together with resonances of the PCL main chain. The methylene hydroxy hydrogens of the PCL end-groups were at 3.66 ppm. The resonance at 5 ppm corresponds to the benzyl hydrogens ($8H_a$), which indicated the direct link between the PCL arms and the initiator core **3c**. The ratio of the integration of the peak at 5 ppm with phenyl hydrogens (4Hc) at 6.70 ppm is 0.5 which is direct evidence that all the hydroxyl benzyl groups are linked to the PCL arms of the initiator **3c**.

Thermal Properties

The thermal properties were evaluated using DSC and TGA (Figure 4). Generally increasing the PCL chain length resulted in increase in the T_m, however there are differences in the Tm depending on the structure of the initiator core. For the smaller PCL arms, the Tm values are comparable to each other. For example, 2cSPL40 has Tm = 49.7 and 3cSPL40 T_m is 49.5. Increasing the feed ratio to 100 resulted in smaller difference of 1 degree, further increase in the length of the PCL arms resulted in 4 ^{o}C in the T_m value. The difference in the T_m could be attributed to the directionality resulting from the rigidity and conformation of the resorcinarence core.

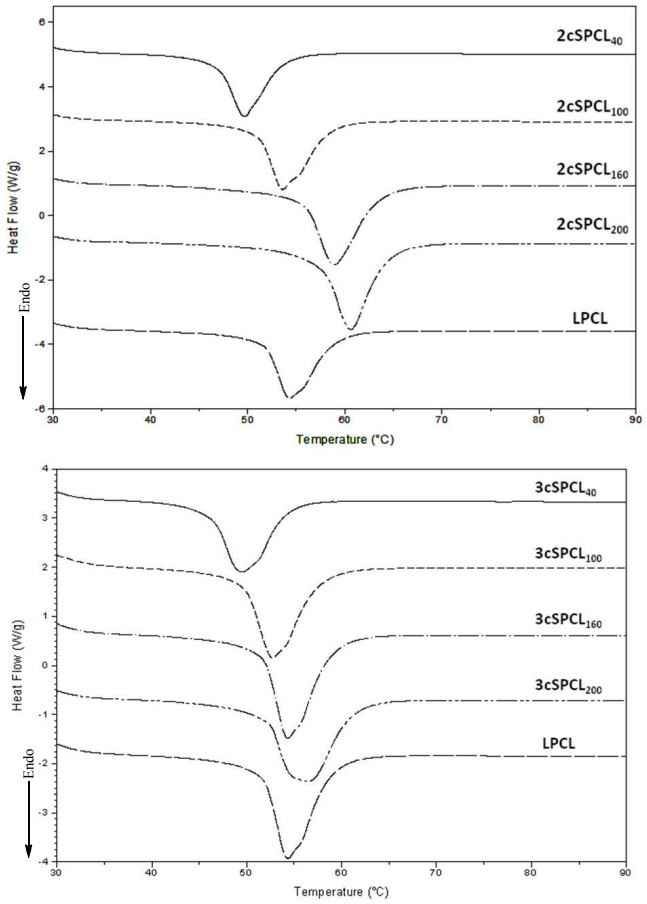


Figure 4. DSC thermograms of directional poly(ε-caprolactone)s (SPCL) based on initiator **2c**, **3c** and Linear Poly(ε-caprolactone).

The presence of a bridge in the upper rim of the initiator **2c** enhances locks its conformation in a rigid crown conformation thus pointing the attached PCL chain in the same direction; the spatial

interaction between the PCL arms results in increased Tm values, relative to the more flexible **3c** due to the absence of the bridge in the upper rim. When compared to the linear polycarpolactone (LPCL) prepared using $Sn(Oct)_2$ as initiator with number-average molecular weight (Mn) of 15400 g/mol, and PDI of 1.5 [Table 1, entry 9] but with without any spatial directionality, the 2cSPCL200 (Table 1, entry 4) of comparable molecular weight has a much higher Tm which is evidence of the effect of spatial directionality on the polymer property (see Figure 4).

TGA analyses were carried out for the synthesized multi-arm polymers and compared to LPCL; the thermal decomposition temperatures (Td) at 10 % weight lost were measured. Td for multi-arm-PCL for the both initiator cores with same feed ratios were similar to each other and increase with increasing the feed. Although the polymers based on **2c** show slightly higher Td values (see Table 1). Similar to the DSC data, polymers based on initiator **2c** have higher Td than those based on initiator **3c** or LPCL. Figure 5 show thermograms of multi-arm PCL based on initiator **2c** and **3c** along with LPCL. Both multi-arm polymers have showed higher Td compare to LPCL. 2cSPCL and 3cSPCL have similar dTG (derivative thermogravimetric) curves with one single narrow pyrolysis peak and the 2cSPCL's degradation temperature is higher than 3cSPCL. The LPCL showed decomposition at lower temperature and its boarder pyrolysis peak suggested that it had lower thermal stability and crystallinity than 2cSPCL and 3cSPCL. The data obtained from the TGA supports the theory of spatial interaction among the PCL arms induced by the resorcinarenes core.

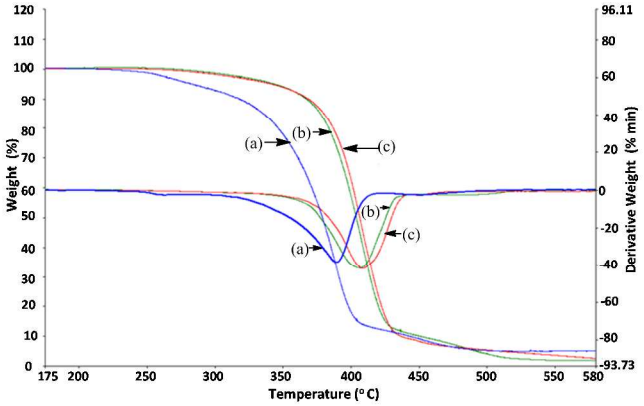


Figure 5. TGA thermograms: (a) LPCL [Table 1, entry 9]. (b) $3cSPL_{200}$ [Table 1, entry 8]. (c) $2cSPL_{200}$ [Table 1, entry 4]

Crystallization Behaviors

Both DSC and TGA indicate that the resorcinarenes initiators **2c** and **3c** induces the spatial interactions between the PCL arms. Therefore, the crystallization behaviors for both mltiarms-polycaprolactone were evaluated by DSC and WAXS along with linear polycaprolactone. The calculation of the percent crystallinity (Xc) based on the enthalpy of melting of 100% crystalline PCL (see experimental section, Table 1). Increasing the PCL arm's length increase the percent crystallinity of the polymers as longer chain tend to pack efficiently and the effect of the floppy chain ends becomes less significant. However, the cavitand resorcinarenes **2c** show higher crystallization than the relatively more flexible structure of **3c** initiator in all feed ratios due the absence of the methylene bridge which lock the conformation and direct the polymer chain in the same direction resulting in increase in crystallinity. The influence of the core becomes more obvious with increasing the length of the PCL arms. For instance, smaller PCL chains of $2cSPL_{40}$ and $3cSPL_{40}$ have similar Xc of 41% and 38%, respectively and increasing the feed ratio to 200, the different in percent Xc increased to 12 % in favor of the multi-arm polymer based on the bridged resorcinarene **2c**. The data suggest that the rigid directional structure of core is influencing the spatial directionality of the PCL arms in $2cSPL_{200}$. Both synthesized multi-arm polymers show higher crystallinity than LPCL of similar molecular weight. The percent crystallinity of LPCL is in agreement with the literature value of 42% determined by small-angle X-ray scattering (SAXS) and NMR.[18]

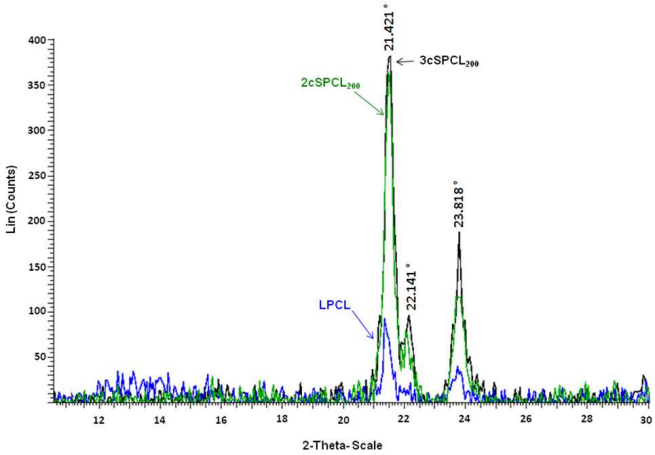


Figure 6. WAXS diffractograms overly of LPCL, $2cSPL_{200}$ and $3cSPL_{200}$.

Further investigation of the crystallinity of the polymers were carried out using wide-angle X-ray scattering (WAXS). WAXS diffractrograms of $2cSPL_{200}$, $3cSPL_{200}$, and LPCL are shown in Figure 6. WAXS pattern shows the same profile of the main peaks with different intensities at 2θ of 21.4° (390), 22.1° (95), and 23.8° (190) for $2cSPL_{200}$, and at 2θ of 21.4° (360), 22.1° (80), and 23.8° (120) for $3cSPL_{200}$. The intensities of the peaks are higher for $2cSPL_{200}$ which indicate higher crystallinity than $3cSPL_{200}$. LPCL shows same main reflections at 2θ of 21.4° (90) 22.1° (20), and 23.8° (40) with much lower intensities. DSC and WAXS data indicate that the crystallinity of the multi-arm PCL based on initiator 2c and 3c increased compared to LPCL with similar molecular weight. The spatial directionality of the polymer chains, a results of the rigid bowl shaped resorcinarene cavitand cores, results in enhanced interaction among the PCL arms resulting in higher thermal stability and crystallinity.

CONCLUSIONS

To conclude, while multiarm polymers such as star and branched are of much interest and have previously been synthesized, no report exist on the effects of spatial directionality on polymer properties. To date most multi-arm/branched polymers either lack spatial directionality or are attached to immovable surfaces. In an effort to evaluate the effects of spatial directionality, we have synthesized tetra-arm poly(e-caprolactone) directional polymers based on resorcin[4]arene by "core first" approach. The spatial directionality was consequence of a rigid bowl shaped resorcinarene cavitand core. The presence of four PCL chains was confirmed by the analysis of the ^{1}H-NMR spectra. The spatial directionality of the PCL chains influenced the thermal properties and crystallinity of the polymers. The T_m, T_d and %*Xc* of the directional PCL form a rigid core cavitand **2c** was significantly higher than that of the linear counterparts ro the somewhat flexible cavitand core **3c**. Importantly, the directional PCL showed much different thermal and crystallization behavior than non-directional star PCL reported in literature. The data implies that the spatial directionality of the polymer chains in multiarm polymers can be used to manipulate their thermal and physical properties.

Experimental

Materials

All reagents were used without further purification unless otherwise 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 form 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 x 10^2, 8.00 x 10^2, 2.10 x 10^3, 4.00 x 10^3, 9.00 x 10^3, 1.90 x 10^4, 5.00 x 10^4, 9.26 x 10^4, 2.33 x 10^5, and 3.00 x 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 performed 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 °C/min and cooling rate of 40 °C/min. The relative crystallinity of samples was calculated according to equation 1:

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

Where *Xc* is the percent crystallinity, ΔH_m is the enthalpy of melting of the sample, and ΔH_m° is the heat of melting of 100% crystalline PCL. The value of ΔH_m° used in the calculation is 136.4 J/g.[14] Thermogravimetric analysis (TGA) measurements were performed with a PerkinElmer STA 6000 Simultaneous Thermal Analyzer (purge gas nitrogen and scan rate of 10°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° to 40° 2θ using a step size of 0.05° 2θ with a collection time of 0.5 per step at 25 °C.

Synthesis of Octol-resorcin[4]arene (1)[15]

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 precipitate was filtered and washed several times with distilled water until it turned neutral to the pH paper. Yield 10.7g (**88** %). MP: >220 °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). ^{13}C 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)[16]

Compound **1** (5g, 5.5 mmol) was dissolved in 55 mL DMF in 125 mL in sure-seal 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 tube was sealed and immersed in a preheated oil bath 80 °C for 24h. The reaction mixture was poured into cold ice water and the white solid was collected by suction 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 octamethoxy resorcinarene (3a)

Compound **1** (5g, 5.6 mol) was dissolved in 50 mL acetone in 125 mL sure-seal tube. Potassium carbonate (12.1 g, 88 mmol) was added and stirred for 0.5 h. Then methyl iodide (5.5 mL, 88 mmol) was added at room temperature. After addition, the reaction mixture was sealed and immersed in preheated oil bath 80 °C for 24h. The tube was cooled in ice water and the solid was filtered off. The compound was crystallized in acetone/methanol mixture. White crystals were obtained. Yield 4.4g (**80** %). mp 109 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 0.76 (t, 12H, J = 6.25Hz), 1.11 (m, 32H), 1.77 (m, 8H), 2.16(s, 12H), 3.43 (s, 24H), 4.37 (t, 4H J = 7.25 Hz), 6.45 (s, 4H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 10.2, 14.1, 22.8, 28.6, 29.6, 31.9, 35.6, 37.5, 59.9, 98.5, 123.4, 124.2, 133.1 155.5.

Synthesis of tetrabromide cavitand (2b)[16]

Compound **2a** (4g, 4.3 mmol) and AIBN (100 mg, 0.6 mmol) were dissolved in 50 mL of degassed benzene. Then NBS (5.4g, 30 mmol) was added and the reaction mixture was refluxed 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 °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 tetrabromo-octamethoxy resorcinarene (3b)

Compound **2a** (4g, 4 mmol) and AIBN (80 mg, 0.5 mmol) were dissolved in 50 mL of degassed benzene. Then NBS (5.4g, 30 mmol) was added and the reaction mixture was refluxed overnight. After completion, the solid precipitate (succinimide) was filtered off and benzene was evaporated. The residue was dissolved in boiling ethanol and let to cool at room temperature. White precipitate was collected. Yield 4.5g (**88** %). mp: >162 °C (decompose). ^{1}H NMR (250 MHz, $CDCl_3$) δ: 0.87 (t, 12H, J = 6.25Hz)), 1.26 (m, 32H), 1.89 (m, 8H), 3.77 (s, 24H), 4.55 (t, 4H J = 7.25 Hz), 4.64 (s, 8H), 6.45 (s, 4H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 14.1, 22.7, 23.9, 26.4, 29.5, 31.8, 36.0, 37.1, 61.6, 125.9, 127.8, 133.6, 156.1

Synthesis of Tetrol cavitand (2c)[17]

Compound **2b** (1g, 0.8 mmol) was dissolved in 40 mL acetone/water (9:1) in sure-seal tube. Then K_2CO_3 (0.3g, 2.2 mmol) was added, and the reaction mixture was immersed in a preheated oil bath at 80 °C

for 24h. After completion, the acetone was evaporated and residue was dissolved in ethyl acetate and extracted with brine solution. The **2C** as a white solid was obtained after purification by silica gel plug eluting with 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.

Synthesis of tetrahydroxy-octamethoxy resorcinarene (3c)
Compound **3b** (1g, 0.76 mmol) was dissolved in 40 mL acetone/water (9:1) in a sure-seal 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 compound was further purified by silica gel plug eluting with 20 % ethyl acetate/hexane. The compound was obtained as white solid. Yield 740 mg (92%), mp = 154 ^{o}C. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 0.80 (t, 12H, J = 6.25Hz)), 1.30 (m, 32H), 1.90 (m, 8H), 3.70 (s, 24H), 3.90 (s, 8H), 4.50 (t, 4H J = 7.25 Hz), 6.70 (s, 4H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 14.1, 22.8, 28.5, 29.6, 31.9, 35.5, 37.2, 56.5, 61.8, 127.2, 129.8, 136.6, 155.6.

General procedure of synthesis of directional poly(ε-caprolactone)s
Resorcin[4]arene initiators (**2c**) or (**3c**) were added into a 15 mL shlenck tube and dried under vacuum at 50^{o}C for 12h. Then, under nitrogen atmosphere, ε-caprolactone was injected into the reaction 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 continued for 24 hours and the product was dissolved in dichloromethane and precipitated in ice-cold methanol.

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Influence of Resorcin[4]arenes Core Structure on the Spatial Directionality of Multi-arm Poly(ε-caprolactone)s

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The spatial directionality of the polymer chains in multi-arm polymers can be used to manipulate their thermal and physical properties. The synthesis of directional poly(ε-caprolactone), based on rigid and flexible resorcin[4]arene initiator core, was accomplished via ring-opening polymerization catalyzed by $Sn(Oct)_2$ in bulk at 120 ^{o}C.