

# Monolayered Organosilicate Toroids and Related Structures: A Phase Diagram for Templating from Block Copolymers

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## EXPERIMENTAL METHODS

Reagents were available commercially and used as received unless otherwise noted. Solvents were dried using activated alumina columns from Innovative Systems. *rac*-Lactide (LA) was received from Purac and recrystallized from dry toluene 3 times prior to use. *N,N*-dimethylacrylamide (DMA) and (-)-sparteine were purified by stirring overnight over CaH<sub>2</sub> and subsequent distillation under reduced pressure. The hydroxy-functionalized alkoxyamine, 2,2,5-trimethyl-3-(4'-p-hydroxymethyl-phenylethoxy)-4-phenyl-3-azahexan and the thiourea catalyst were prepared according to literature procedures.<sup>1</sup> The PDMA macroinitiator synthesized by nitroxide-mediated polymerization (NMP) was dried in a vacuum oven and further dried by co-evaporation with dry, distilled toluene 3 times before transferring to a glovebox for assembly of the ROP reaction. <sup>1</sup>H-NMR spectra were obtained on a Bruker Avance 400 instrument at 400 MHz. Gel permeation chromatography was performed in THF

using a Waters chromatograph equipped with four 5  $\mu\text{m}$  Waters columns (300 mm  $\times$  7.7 mm) connected in series with increasing pore size (10, 100, 1000,  $10^5$ ,  $10^6$  Å), a Waters 410 differential refractometer and a 996 photodiode array detector, and calibrated with polystyrene standards (750-2  $\times$   $10^6$  g mol<sup>-1</sup>).

#### *SYNTHESIS OF HYDROXY-FUNCTIONALIZED PDMA<sub>70</sub>*

2,2,5-Trimethyl-3-(4'-p-hydroxymethylphenylethoxy)-4-phenyl-3-azahexane (0.20 g, 0.6 mmol), TEMPO (4.2 mg, 0.03 mmol) and *N,N*-dimethylacrylamide (5.10 g, 51 mmol) were stirred at 125 °C for 18 hours and subsequently cooled to room temperature. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and precipitated in diethyl ether (2  $\times$ ) to give 4.15 g (78%) of hydroxyl-functionalized poly(*N,N*-dimethylacrylamide). <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  = 7.24-7.06 (m, 9 H; H<sub>aromatic</sub>), 4.81 (bs, 1 H; HC-ON), 4.62 (bs, 2 H, PhOCH<sub>2</sub>), 3.22-0.42 (m, 650 H; N(CH<sub>3</sub>)<sub>2</sub> PDMAA backbone, CH<sub>2</sub> PDMAA backbone, CH PDMAA backbone, ON-CH, CH<sub>3</sub> initiating fragment, CH<sub>3</sub>CHCH<sub>3</sub>, C(CH<sub>3</sub>)<sub>3</sub>, CH<sub>3</sub>CHCH<sub>3</sub>, CH<sub>3</sub>CHCH<sub>3</sub>). GPC (RI): M<sub>n</sub> (PDI): 7000 g mol<sup>-1</sup> (1.09).

#### *SYNTHESIS OF PDMA<sub>70</sub>-PLA<sub>150</sub>*

A solution of 250 mg (36  $\mu\text{mol}$ ) hydroxyl-functionalized poly(*N,N*-dimethylacrylamide), 198 mg (536  $\mu\text{mol}$ ) thiourea-catalyst, 60 mg (268  $\mu\text{mol}$ ) (-)-sparteine and 770 mg (5.36 mmol) *rac*-lactide (LA) were stirred in 7.5 ml dry methylene chloride for 3 hours. The resulting viscous solution was diluted with CH<sub>2</sub>Cl<sub>2</sub> and precipitated in pentane (2  $\times$ ). The white precipitate was collected by filtration. Isolated yield: 1.03 g (95%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  = 7.24-7.06 (m, 9 H; H<sub>aromatic</sub>), 5.22-5.08 (m, 303 H; CH<sub>PLA</sub>, HC-ON, PhOCH<sub>2</sub>), 4.38-4.18 (m, 2 H; CHOH, CHOH) 3.22-0.42 (m, 1250 H; N(CH<sub>3</sub>)<sub>2</sub> PDMAA, CH<sub>2</sub> PDMAA, CH PDMAA, CH<sub>3</sub> PLA, ON-CH, CH<sub>3</sub> initiating fragment, CH<sub>3</sub>CHCH<sub>3</sub>, C(CH<sub>3</sub>)<sub>3</sub>, CH<sub>3</sub>CHCH<sub>3</sub>, CH<sub>3</sub>CHCH<sub>3</sub>). GPC (RI): M<sub>n</sub> (PDI): 47100 g mol<sup>-1</sup> (1.11).

## MORPHOLOGY DIAGRAM

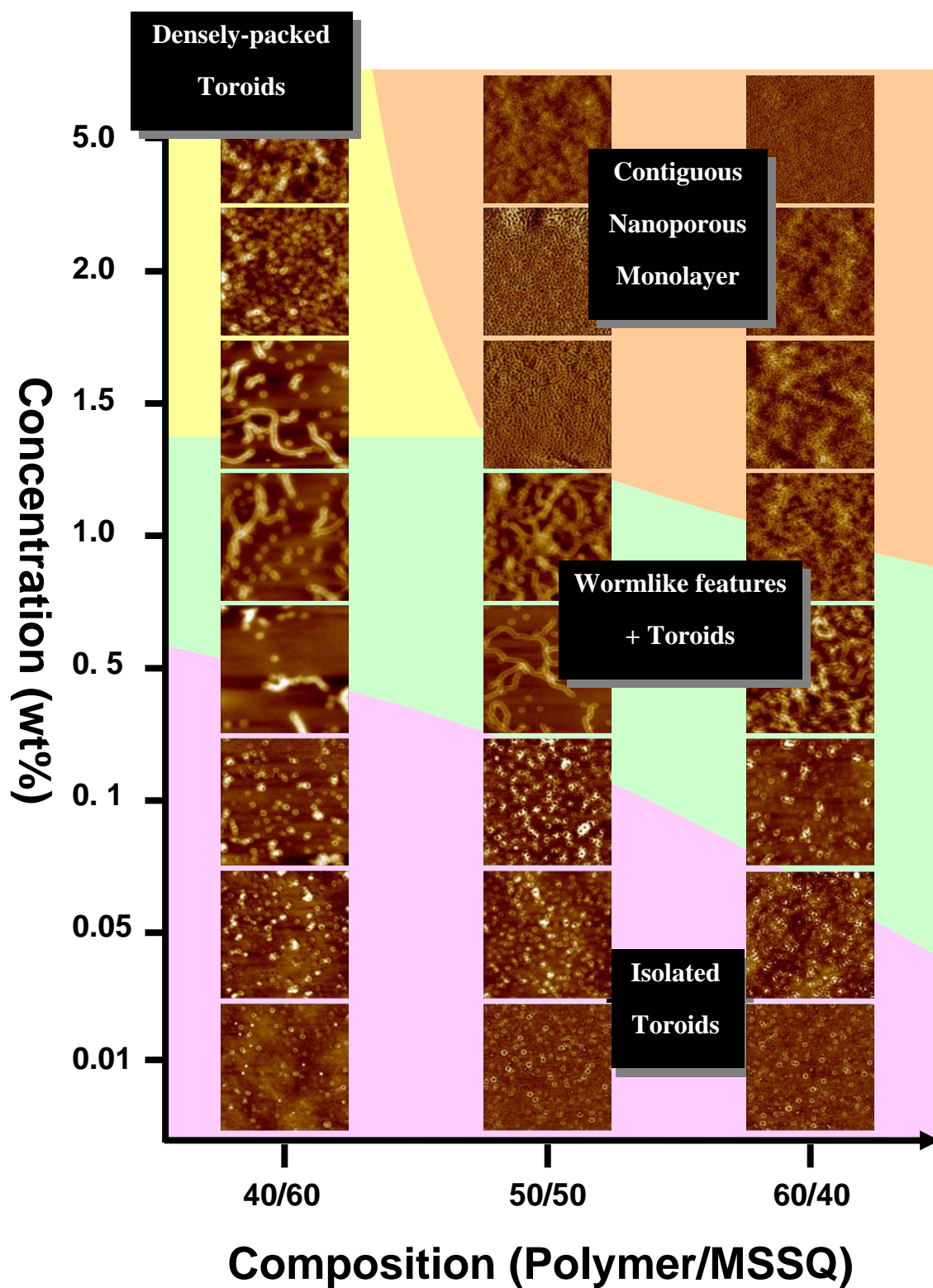
Figure S1 shows the morphology diagram of micelle-templated nanostructures prepared by depositing poly(*N,N*-dimethylacrylamide-*b*-lactide) copolymer (PDMA-PLA) and methyl silsesquioxanes (MSSQ) mixture solution in propylene glycol propyl ether (PGPE) onto a silicon wafer surface using different mixture compositions and solution concentrations. Atomic force microscopy (AFM, Dimension 3100, Digital Instrument) in tapping mode was applied for characterization of the morphology of nanostructures formed using standard silicon cantilevers (Veeco OTESPA, frequency range 267-331 kHz), and AFM images corresponding to each sample are provided in Figure S1. AFM images for 1.5 and 2.0 wt% of 50/50 samples and 5.0 wt% of 60/40 sample are phase images ( $z$  range: 10 ~ 20°), and all the other images are height images with  $z$  range varying from 10 to 40 nm.

## MICROSCOPIC OBSERVATION OF PROBABLE TOROIDAL FUSION

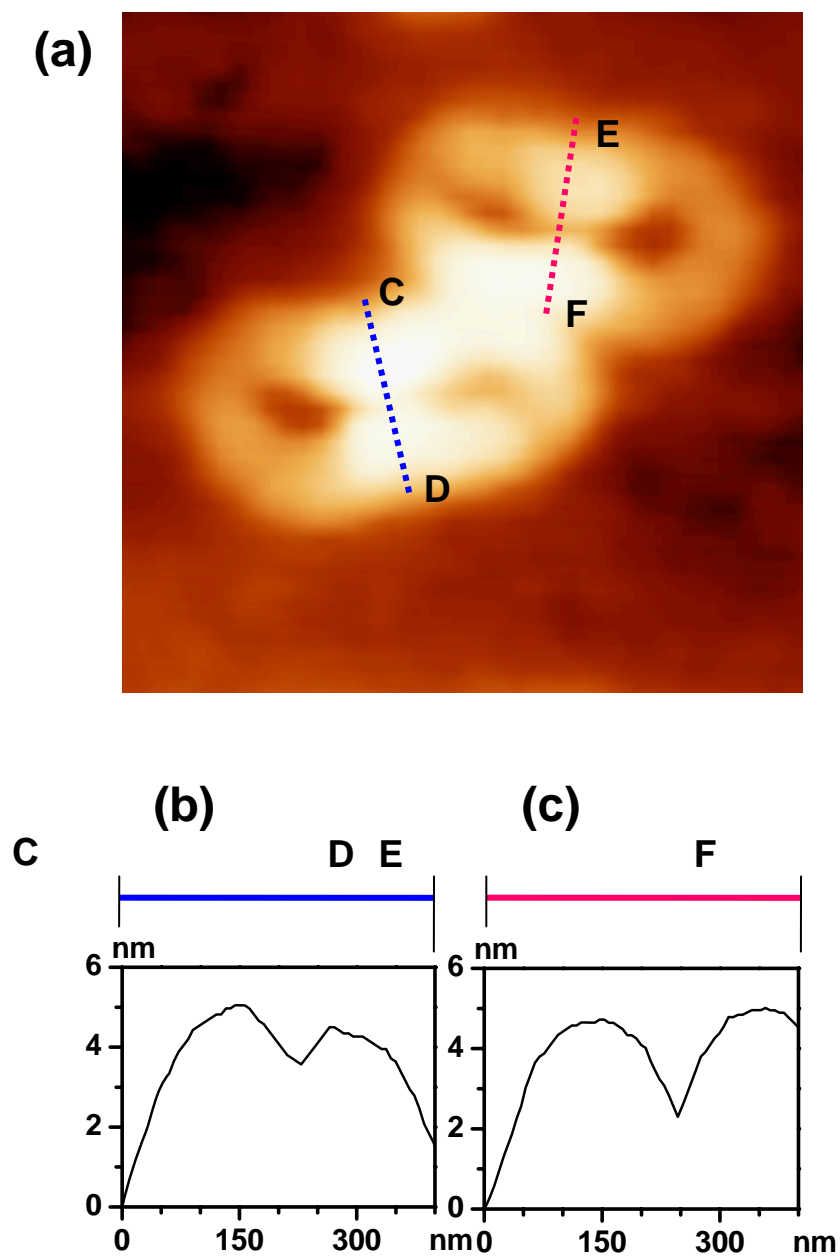
As reflected in the height profile in Figure 2b, the outer and inner diameters of the wormlike features are found to exactly match with those of the toroids, implying that they transform into each other. Figure S2a is a zoom image taken from the box in Figure 2a, where the proposed intermediate stage of fusion of toroids is shown. Figures S2b and S2c show the height profiles taken from lines C-D and E-F in Figure S2a, respectively.

## REFERENCES

- (1) Bosman, A. W.; Vestberg, R.; Heumann, A.; Frechet, J. M. J.; Hawker, C. J. *J. Am. Chem. Soc.* 2003, *125*, 715-728.



**Figure S1.** Morphology phase diagram of nanostructures with all corresponding AFM images ( $1.5\ \mu\text{m} \times 1.5\ \mu\text{m}$ ).



**Figure S2.** (a) Zoomed image taken from the box in Figure 2 (a) and height profiles corresponding to the lines (b) C-D and (c) E-F.