The Structure-Self-Assembly Relationship in PDMAEMA/Polyester Miktoarm Stars

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Figure S1. ATR-IR spectra of linear copolymers

Table S1. Characterization of linear MI

	DP $_{CL}$	DP $_{LA}$	DP $_{GA}$	$M_{n, calc}$	$M_{n, SEC}{}^{c}$	Đ^{c}
MI1	-	112	-	8 100^{b}	11 200	1.24
MI2	93	-	-	10 600^{b}	21 100	1.38
MI3	-	84	30	7 800^{b}	8 500	1.51
MI4	17	94	24	10 100^{b}	15 000	1.55

a – calculated from GC chromatograms, b – calculated from ^{1}H NMR spectra, c – THF as an eluent and PS standards.
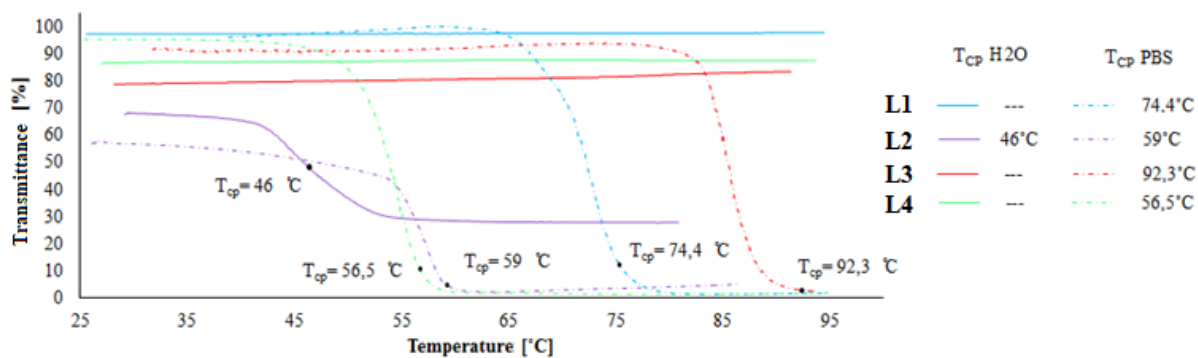

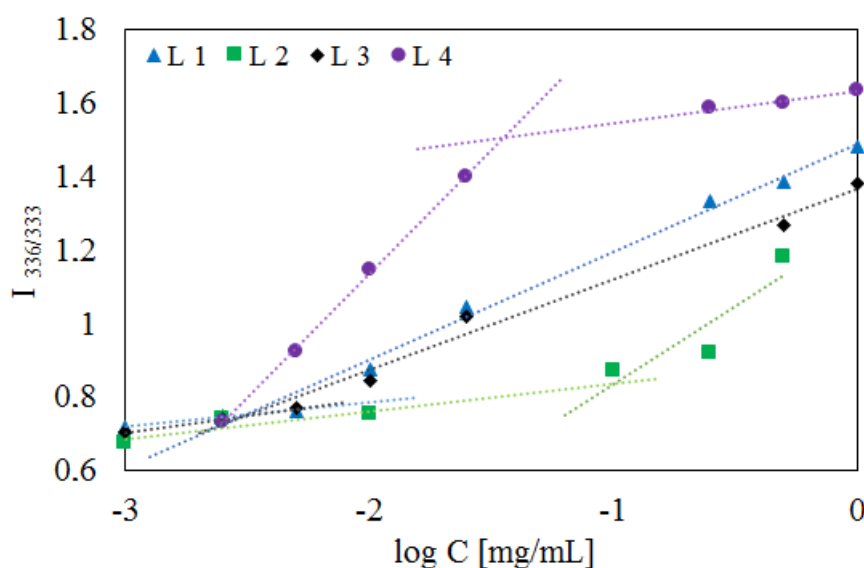**Figure S2.** The plots of transmittance vs temperature for linear copolymers.

Figure S3. Plot of intensity versus logC for linear polymers

Table S2. Characterization of linear polymers via measurement of D_h in deionized water

Deionized H_2O					
No.	D_h. 25°C	PdI	D_h. T_{CP} [°C]	PdI	T_{CP} [°C]
L1	257	0.53	-	-	x
L2	294	0.35	275	0.36	46
L3	480	0.53	-	-	x
L4	169	0.28	-	-	x

Where: x –soluble in water but lack of T_{CP}, thus D_h at T_{CP} was not measured

Table S3. Characterization of linear polymers via measurement of D_h in 0.01M PBS (pH 7.4)

0.01M PBS, pH 7.4					
No.	D_h. 25°C	PdI	D_h. T_{CP} [°C]	PdI	T_{CP} [°C]
L1	750	0.55	266	0.10	74
L2	399	0.38	699	1.00	59
L3	885	0.51	-	-	x
L4	657	0.92	190	0.29	57

Where: x –soluble in water but lack of T_{CP}, thus D_h at T_{CP} was not measured

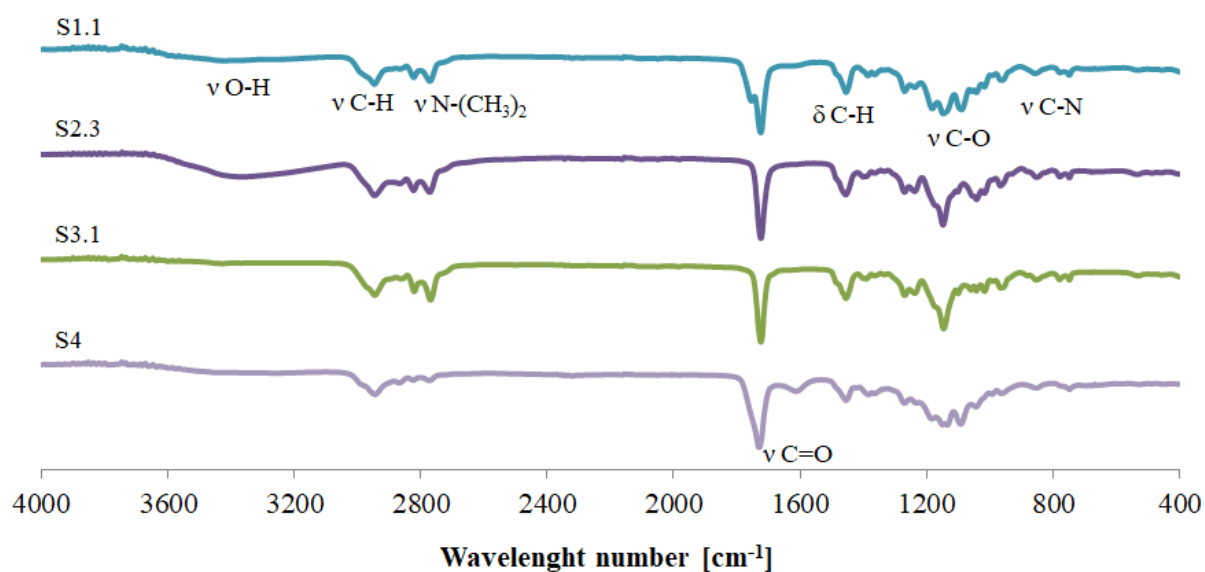## 2. Characterization of miktoarm star-shaped polymers and their precursors

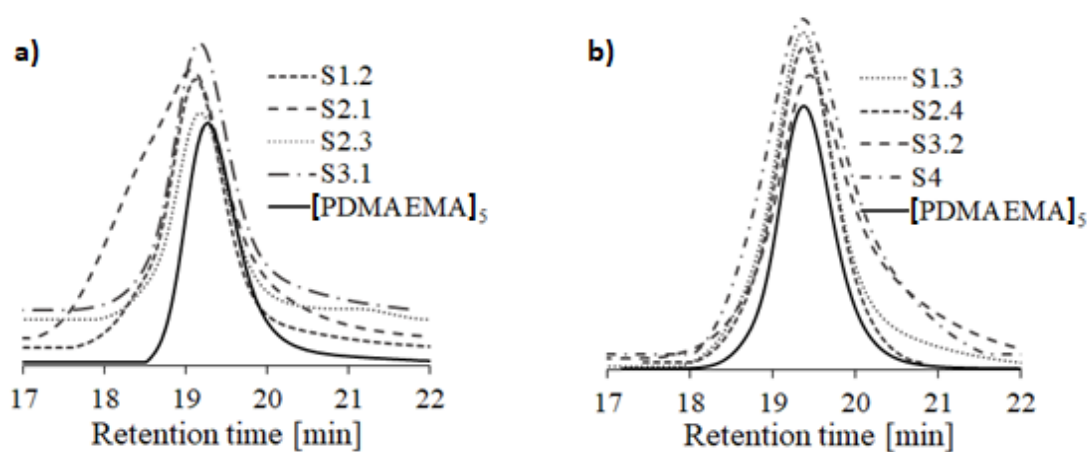**Figure S4.** ATR-IR spectra of chosen miktopolymers

Figure S5. SEC traces of miktoarm star-shaped copolymers where $DP_{DMAEMA}=160$ (A) and $DP_{DMAEMA}=110$(B).
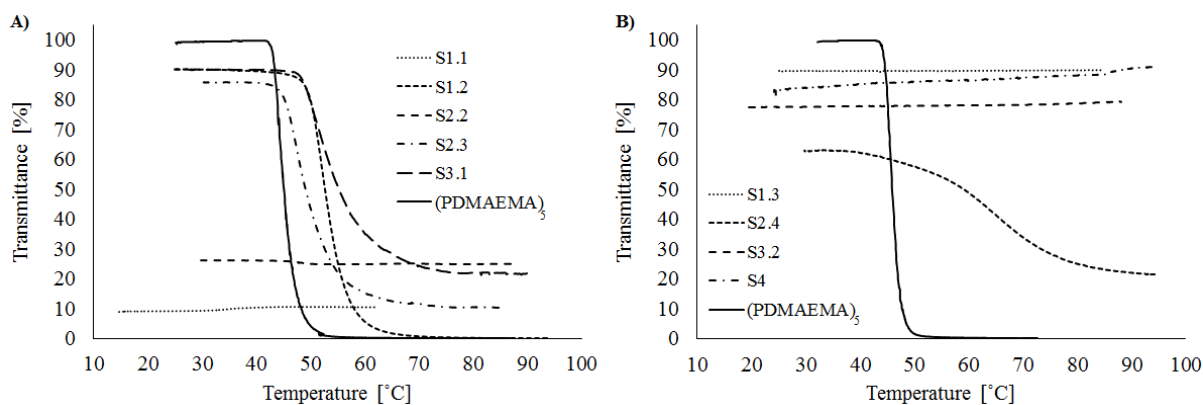
Figure S6. Phase transition of star-shaped miktoarm polymers where $DP_{DMAEMA} = 160$ (A) and with $DP_{DMAEMA} = 110$ (B), in deionized water
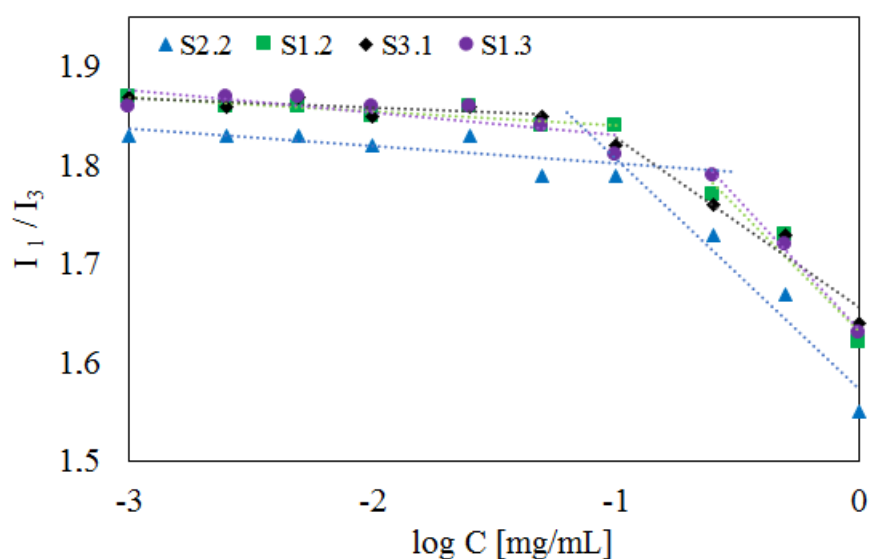

Figure S7. Plot of intensity vs logC for miktopolymers

Table S4. Characterization of polymers used for click reactions

	DP $_{DMAEMA}$	DP $_{CL}$	DP $_{LA}$	DP $_{GA}$	M$_{n,\ calc}$	M $_{n,\ SEC}$[c]	Đ[c]
5-arm PDMAEMA1	160	-	-	-	25 154[a]	22 500	1.28
5-arm PDMAEMA2	110	-	-	-	17 293[a]	19 500	1.14
PLA	-	-	13	-	937[b]	1 200	1.29
	-	-	135	-	9 729[b]	15 900	1.27
PCL	-	15	-	-	1 712[b]	2 800	1.30
	-	68	-	-	7 762[b]	16 400	1.25
	-	115	-	-	13 126[b]	27 700	1.61
PLGA	-	-	10	8	1 185[b]	9 400	1.67
PLGCL	-	96	34	85	18 341[b]	14 200	1.78

Where: a – calculated from GC chromatograms, b – calculated from ^{1}H NMR spectra, c – THF as an eluent and PS standards.

Table S5. Characterization of miktoarm star-shaped polymers via measurement of Dh in deionized water or 0.01M PBS (pH 7.4)

No	Polyester	DP_{DMAEMA} / $DP_{Polyester}$	$F_{hydrophylic}$ [mol%]	$D_{h, H2O}$ 25°C	$D_{h, H2O} T_{CP}$ [°C]	$D_{h, PBS}$ 25°C	$D_{h, PBS} T_{CP}$ [°C]
S1.1	PLA	**160/135**	**0.54**	**208±85**	**252±63**	**243±90**	**550±92**
S1.2		**160/13**	**0.92**	**9±2**	**245±48**	**12±2**	**347±74**
S1.3		110/13	0.89	245±36	n.d.	10±1	420±76
S2.1	PCL	160/115	0.42	n.d.	n.d.	n.d.	n.d.
S2.2		160/68	0.70	172±92	217±61	113±33	610±98
S2.3		160/15	0.91	226±94	161±61	196±151	702±127
S2.4		110/15	0.88	104±40	n.d.	162±50	941±163
S3.1	PLGA	**160/10/8**	**0.90**	**9±1**	**141±32**	**8±1**	**437±74**
S3.2		110/10/8	0.86	290±190	n.d.	337±115	448±75
S4	PLGCL	110/34/85/96	0.34	64±12	n.d.	147±85	407±70

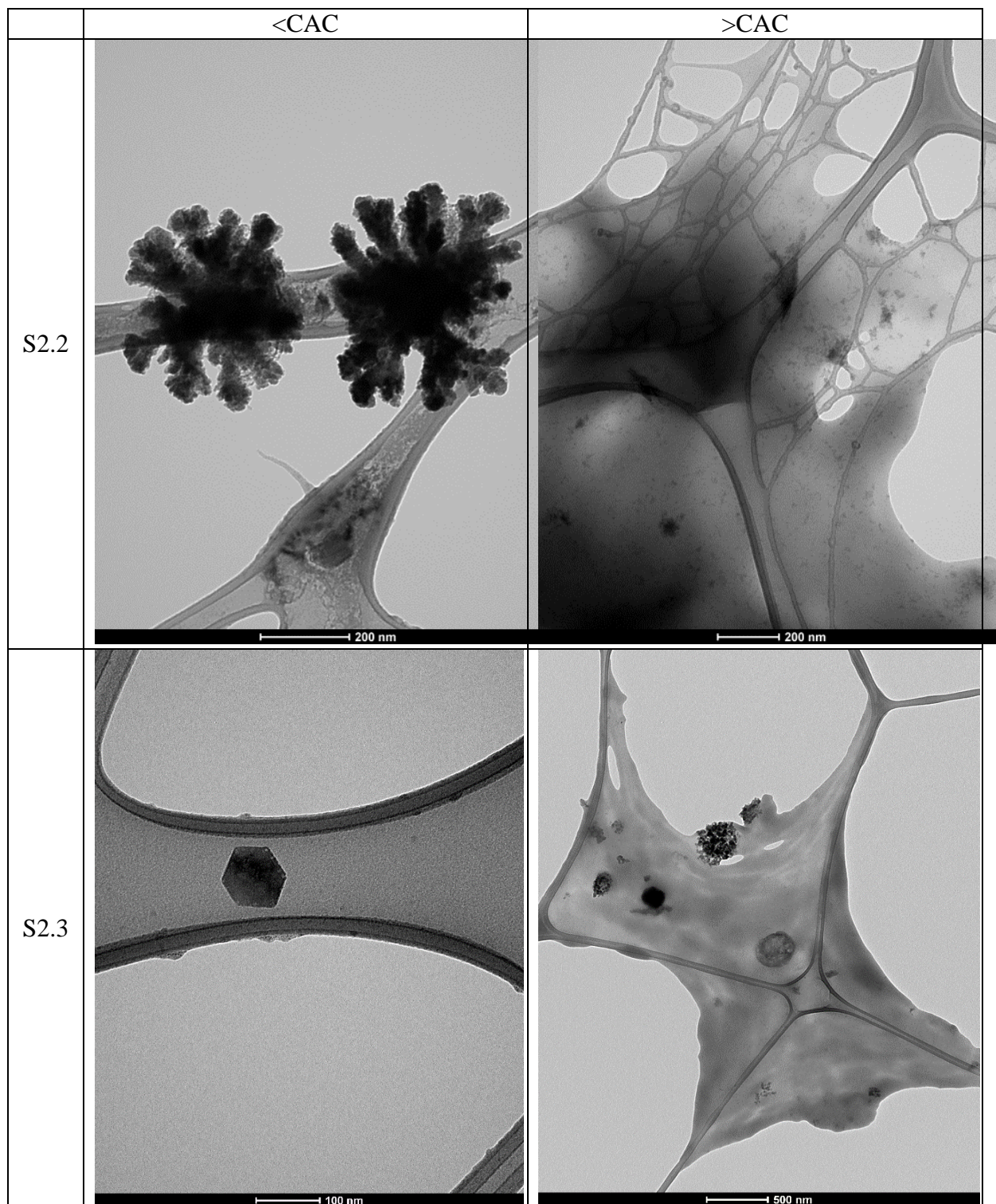Where: n.d.- not determined; the bold corresponds to the polymers where fractal formation has been observed

	<CAC	>CAC
S2.2	200 nm	200 nm
S2.3	100 nm	500 nm

Figure S8. TEM images of miktoarm star-shaped polymers with PCL arm.

	<CAC	>CAC
S1.2		
S1.3		
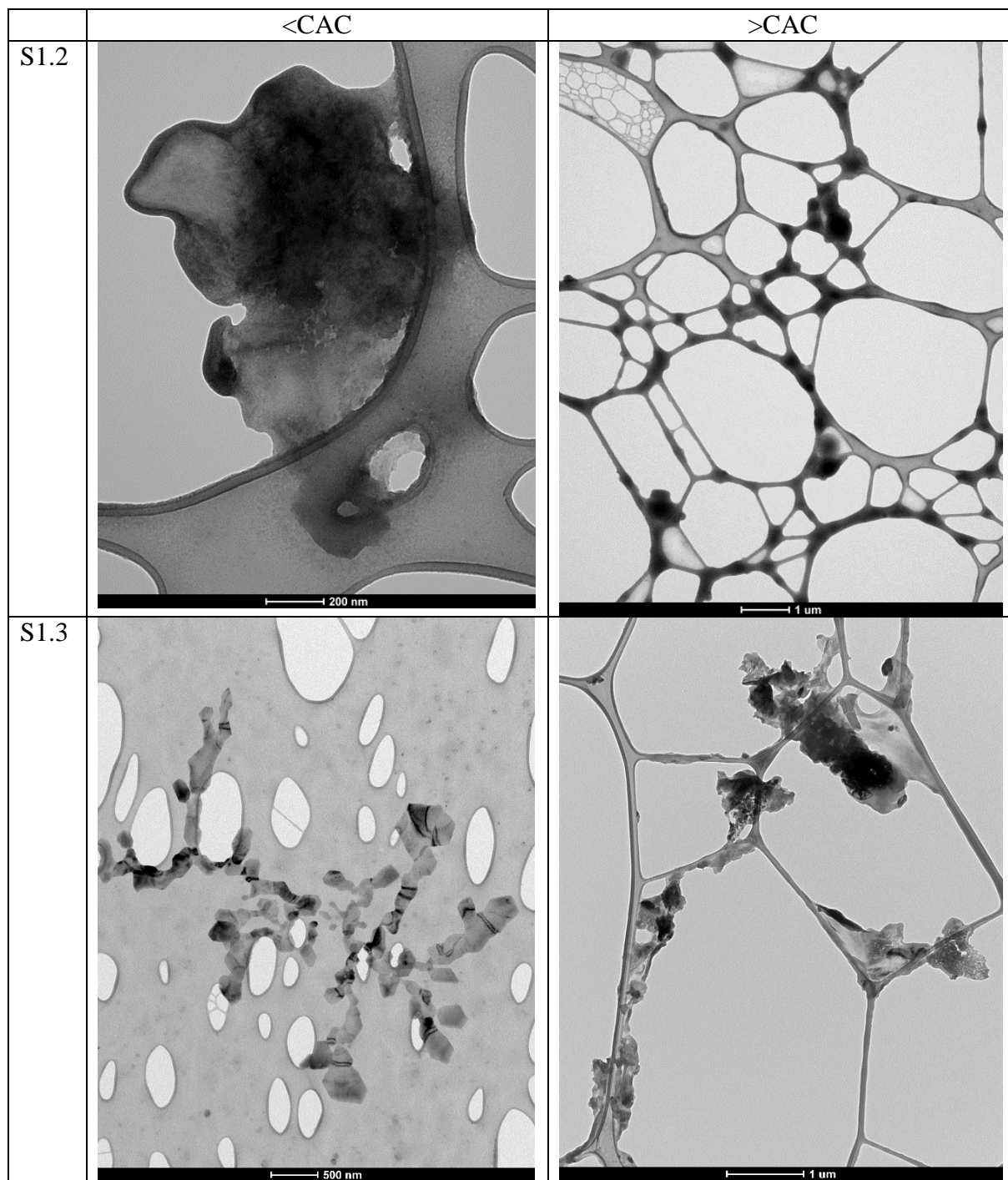
Figure S9. TEM images of miktoarm star-shaped polymers with PLA arm.

	<CAC	>CAC
S3.1		
S3.2		
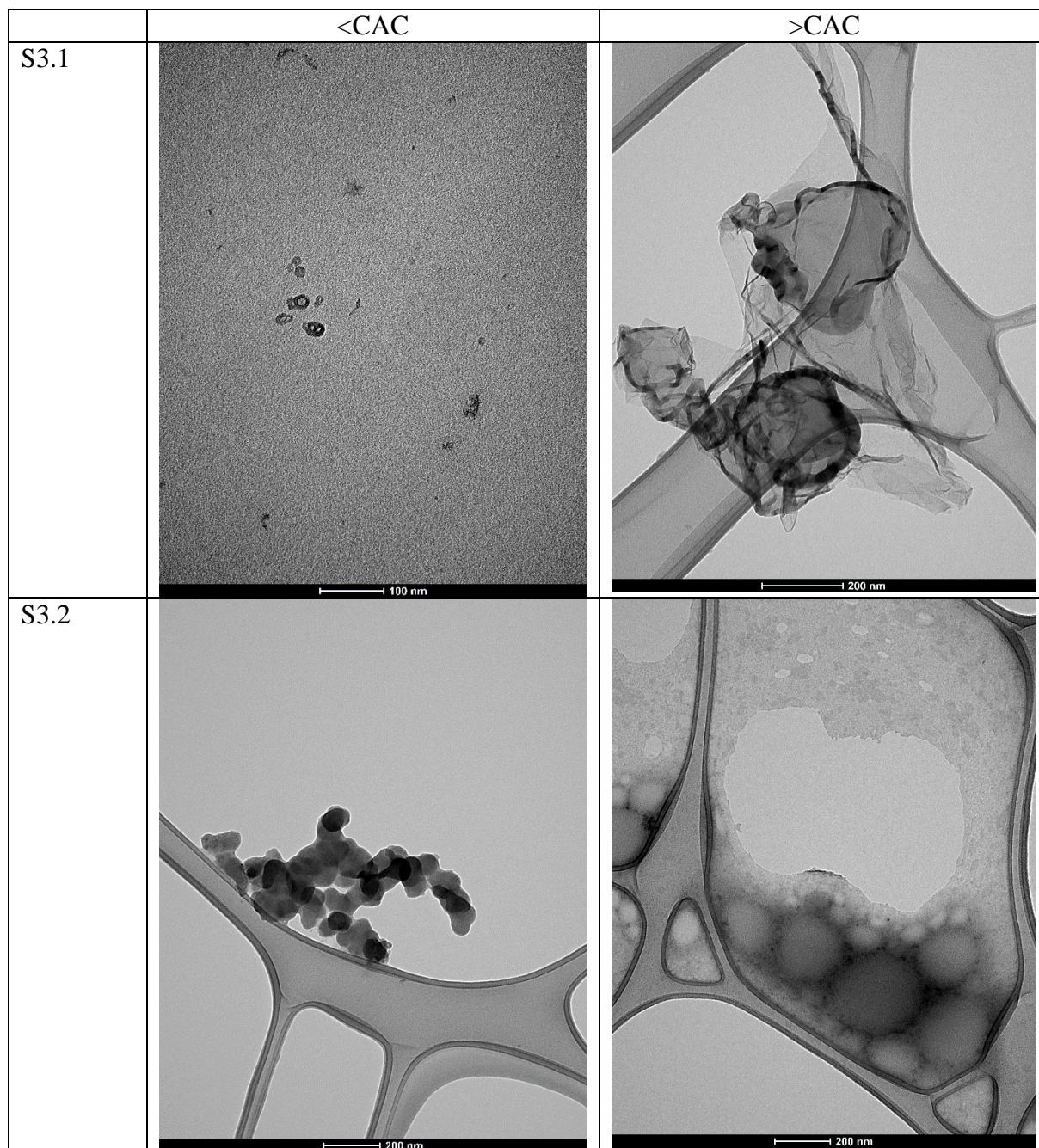
Figure S10**.** TEM images of miktoarm star-shaped polymers with PLGA arm.
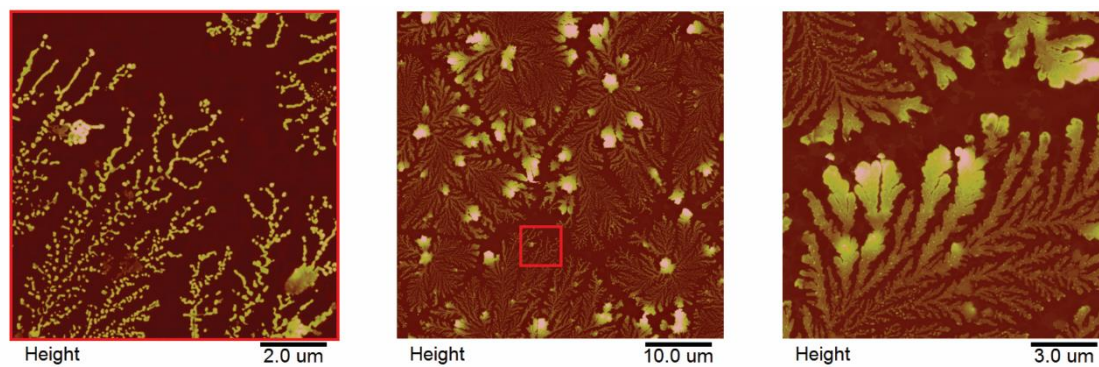
Figure S11. AFM images of S1.1.
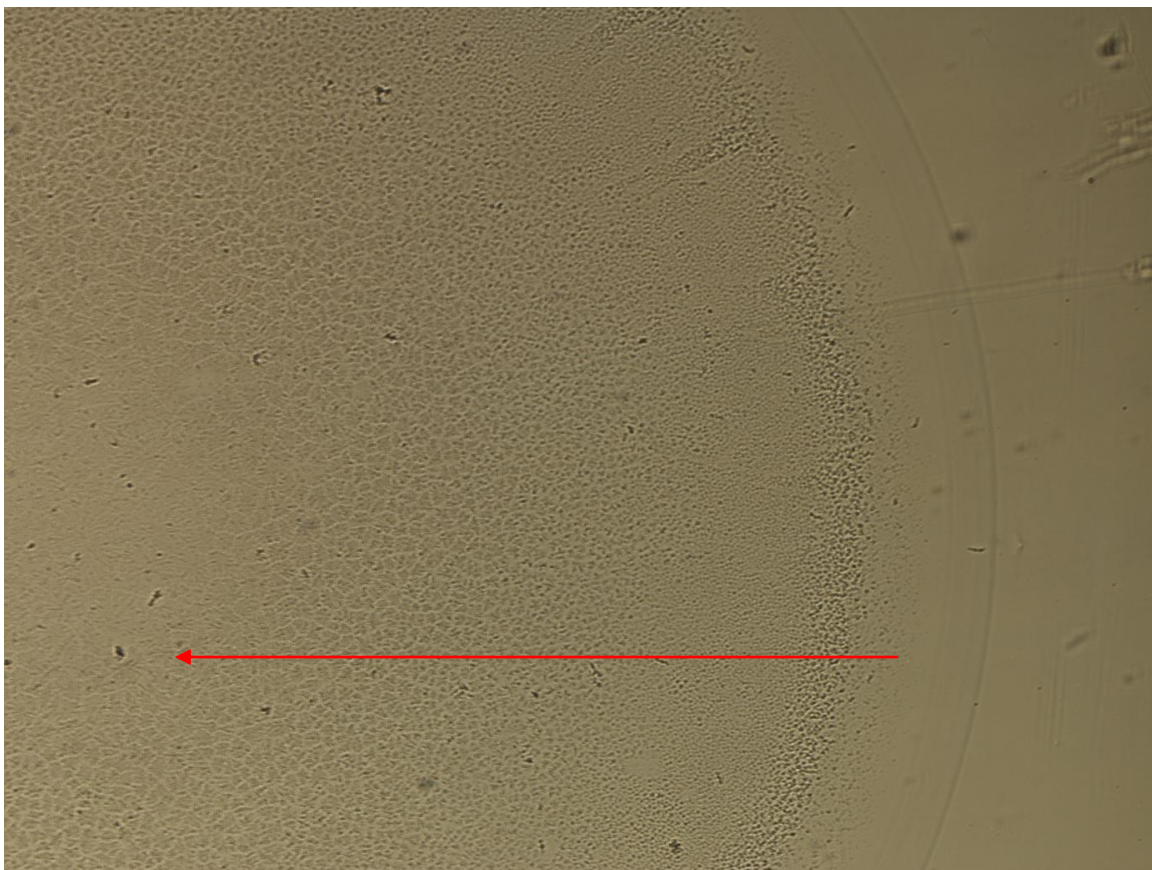
Figure S12. The optical image of S1.2 polymer on mica representing the different drop areas corresponding to different drying time, from the external circle to the center.
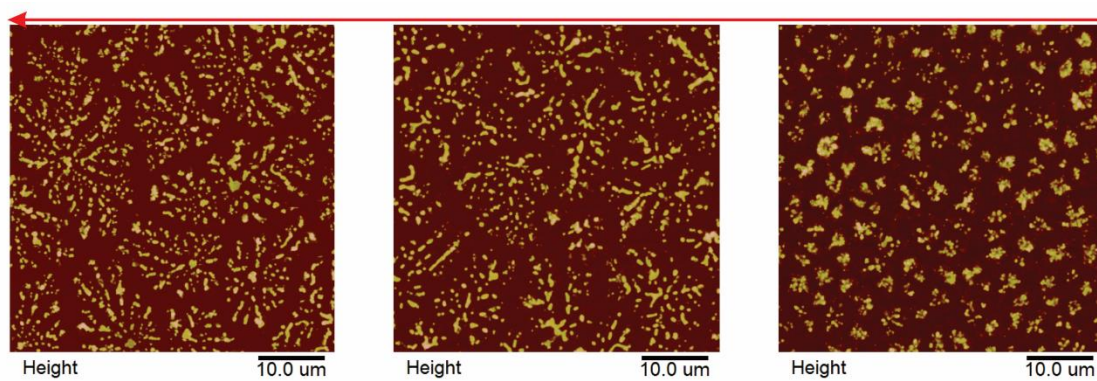

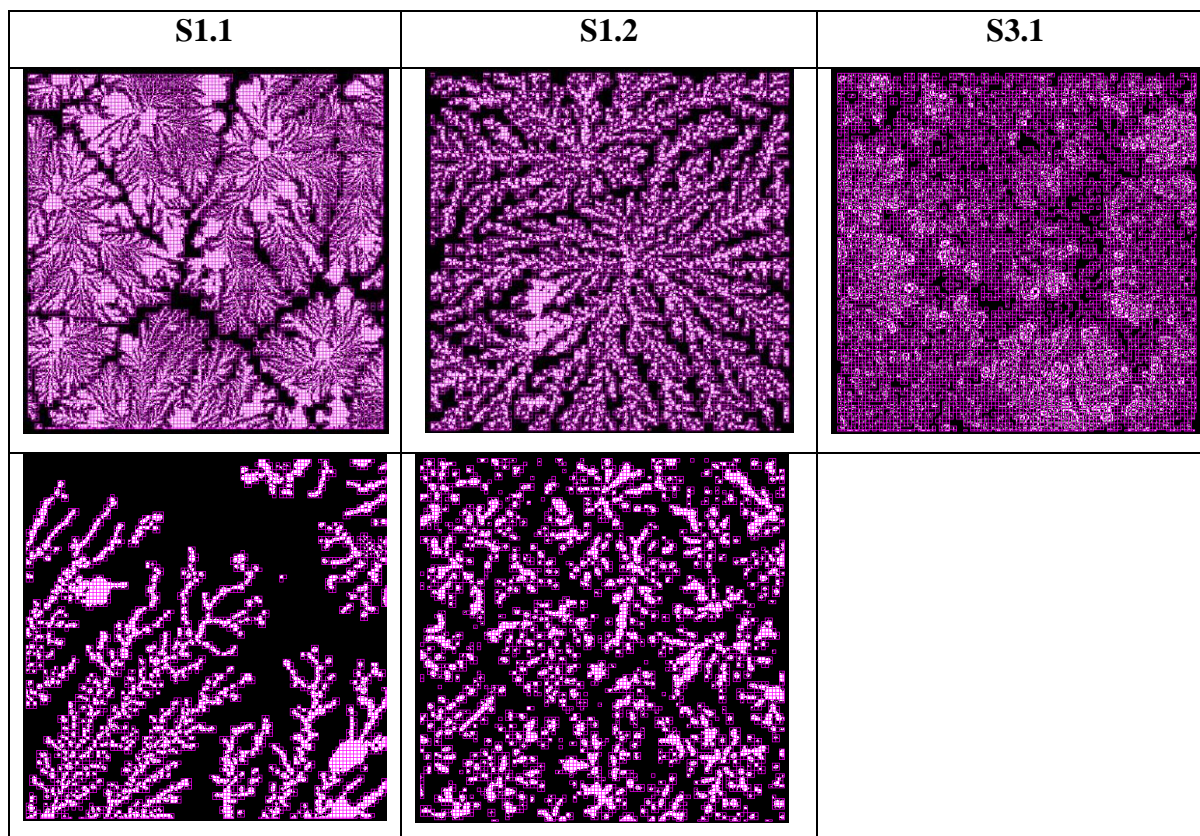**Figure S13.** AFM images of S1.2 polymer representing the size difference of the polymer clusters from different areas of the drop.

S1.1	S1.2	S3.1

Figure S14. Fractal analysis was performed on AFM scans of S1.1, S1.2 and S3.1 using ImageJ software) [1] ((version 1.53k, National Institute of Health, Bethesda, MD, USA). Binarized 8-bit images were used for calculation of fractal dimension (D_f) using FracLac plug-in [2] by Box-counting method with the following settings: number of positions for grids = 1, binary scale; graphics options ticked: regression and draw grids.
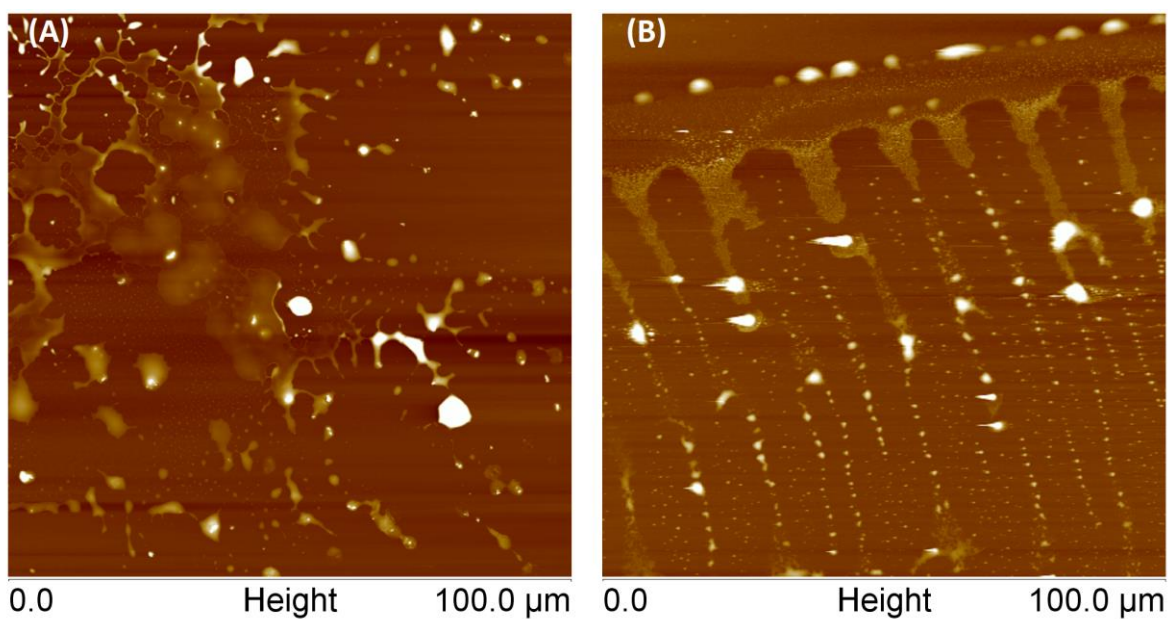

Figure S15. AFM images of S1.2 at initial concentration 0.001 mg/mL at room temperature (A) and at 50 °C (B).
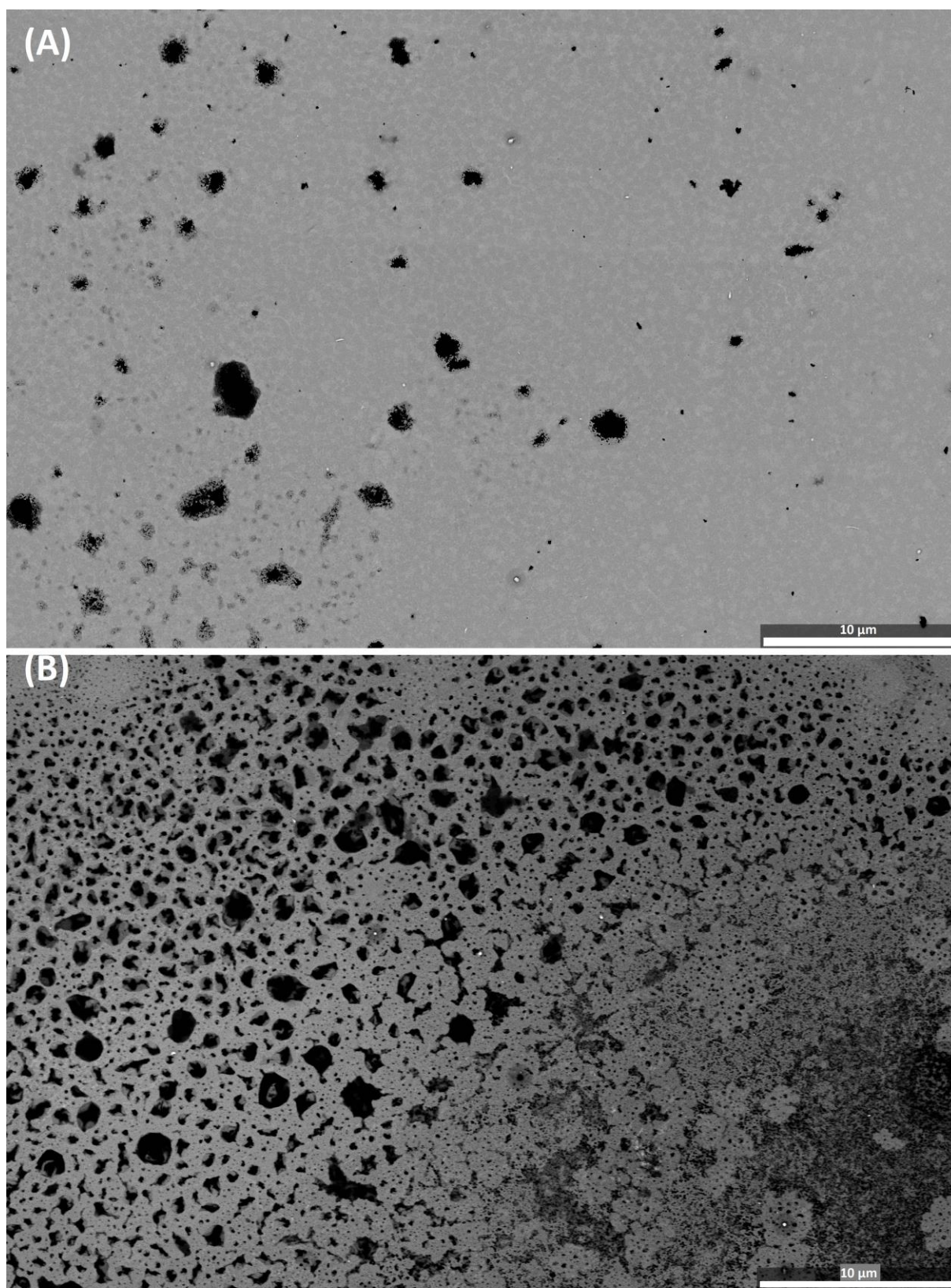
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Figure S16. STEM images of S1.2 (A) and S3.1 (B) at initial concentration equal 0.001 mg/mL.
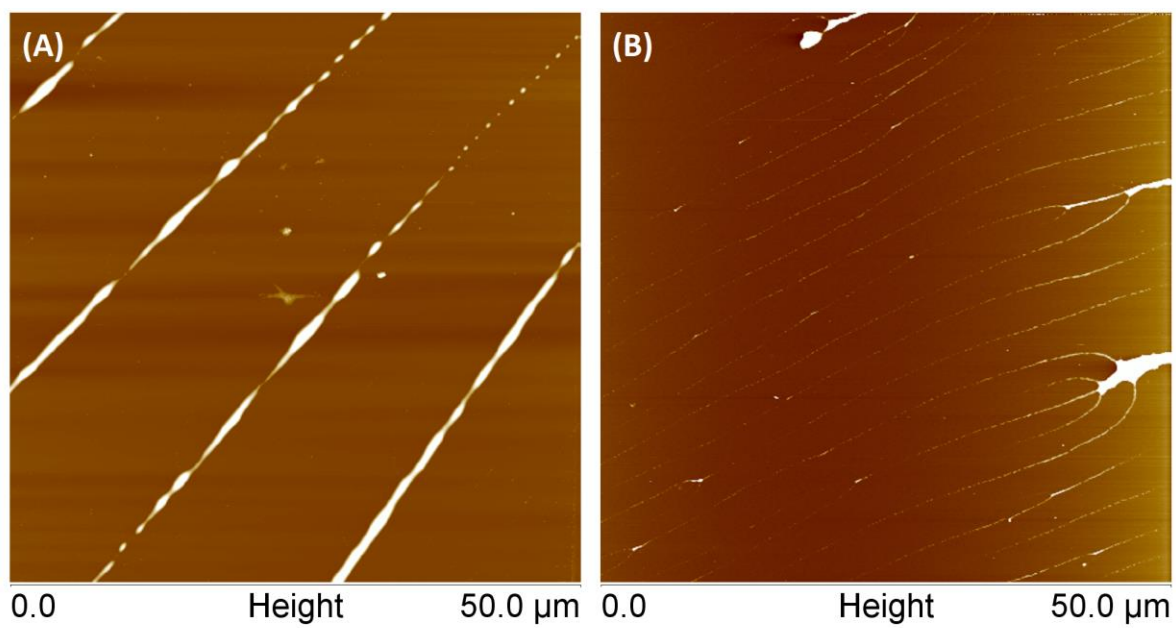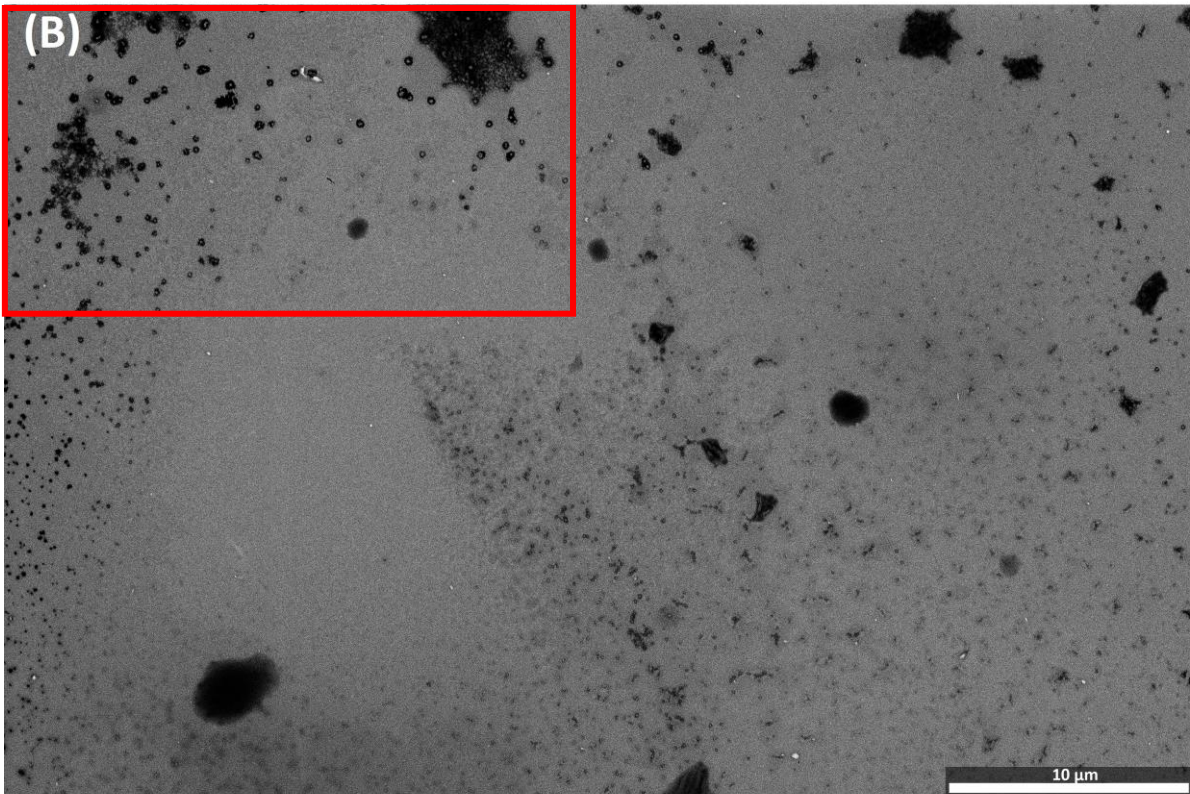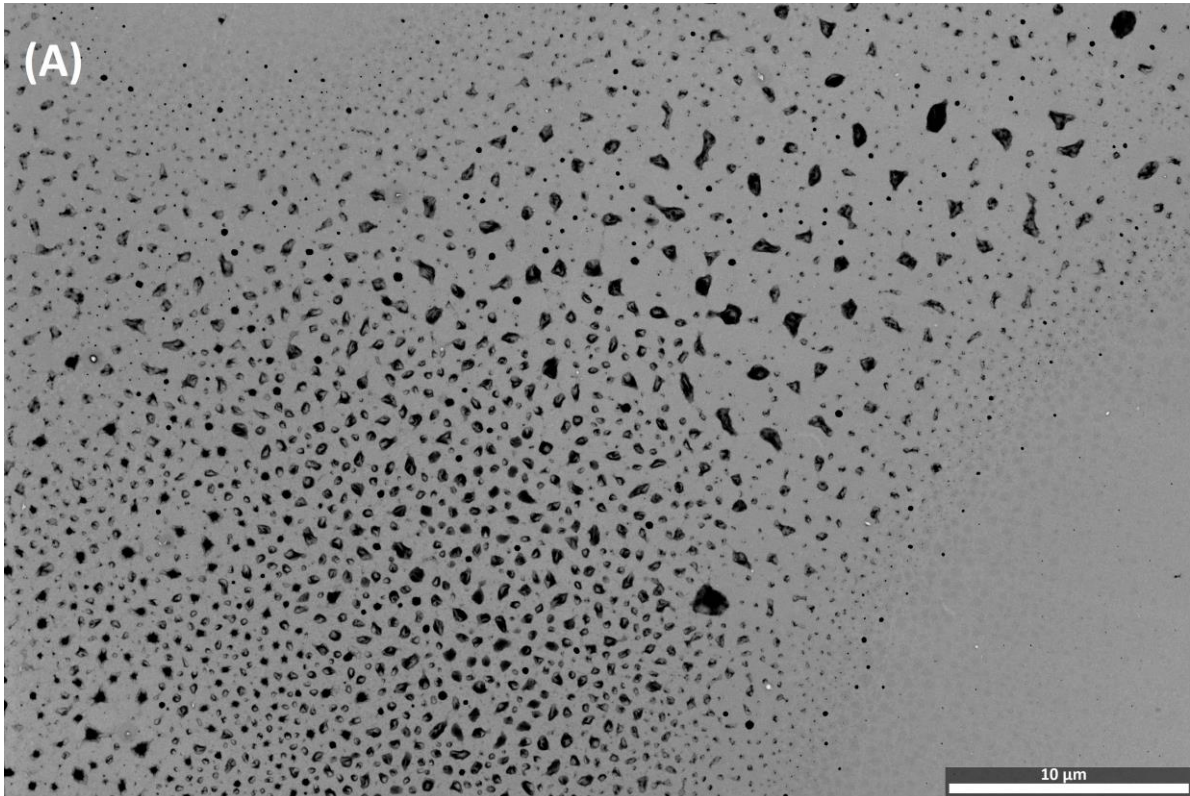
Figure S17. AFM images of S1.2 (A) and S3.1 (B) at 50 °C and initial concentration equal 0.01 mg/mL. The images were taken on the edge formed by a drying drop.
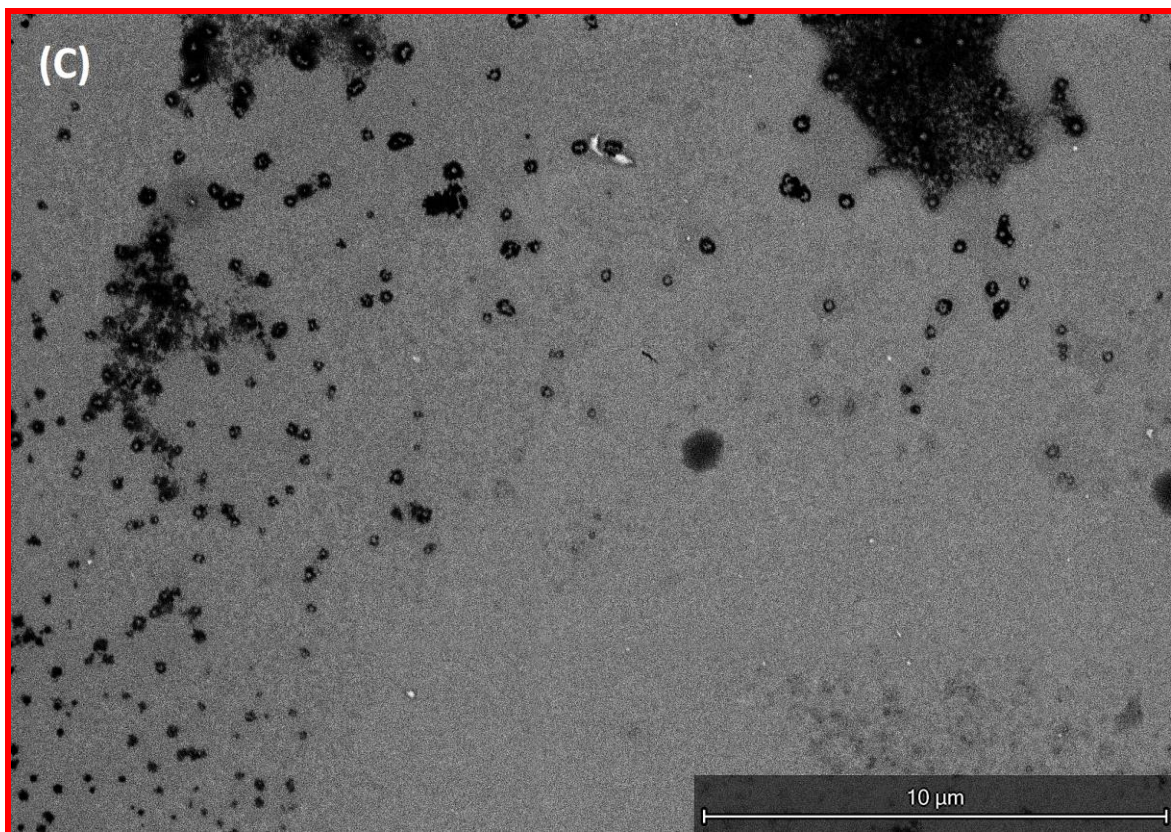
(A)

10 µm

(B)

10 µm

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Figure S18. STEM images of S1.2 (A) and S3.1 (B, C) at 50 °C and initial concentration equal 0.01 mg/mL.

3. Literature

[1] Rasband, W.S., ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, https://imagej.nih.gov/ij/ 1997-2018.

[2] Karperien, A., FracLac for ImageJ, https://imagej.nih.gov/ij/plugins/fraclac/FLHelp/Introduction.htm; 1999-2013.