

Effect of Formulation on the Binding Efficiency and Selectivity of Precipitation MIPs

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Electronic Supplementary Information

Table S1. Imprinting results of polymers synthesized from various template:functional monomer (TM), functional monomer:cross-linker (MX) and initiator:total monomer (IM) ratios.

Experiments		Incorporated components in the polymers			Polymer Composition T :FM : XL ¹	Degree of Cross-linking ²	Hydro-dynamic size, d_H (PDI)
		% incorporation (μmol)					
		EGDMA	MAA	Template			
TM2	MIP _{CAF}	90 ± 1 (375)	79 ± 1 (66)	70 ± 1 (29)	0.44:1:6	68.1 ± 0.01	66 ± 1 (1.0)
	MIP _{THP}	92 ± 1 (382)	75 ± 1 (63)	76 ± 1 (32)	0.51:1:6	62.3 ± 0.01	70 ± 1 (1.0)
	NIP	83 ± 7 (347)	75 ± 2 (62)		1:5.58	70.3 ± 0.06	104 ± 1 (0.4)
TM4/ MX5/ IM100³	MIP _{CAF}	89 ± 2 (369)	80 ± 2 (67)	18 ± 1 (4)	0.06:1:5.53	71.0 ± 0.01	114 (0.3)
	MIP _{THP}	85 ± 2 (359)	77 ± 1 (64)	49 ± 2 (10)	0.16:1:5.10	69.7 ± 0.01	100 ± 1 (0.3)
	NIP	92 ± 2 (384)	80 ± 1 (67)		1:5.77	71.0 ± 0.01	93 ± 1 (1.0)
TM6	MIP _{CAF}	87 ± 2 (362)	74 ± 3 (62)	35 ± 1 (5)	0.08:1:5.85	63.3 ± 0.01	99 ± 2 (0.)
	MIP _{THP}	90 ± 2 (373)	77 ± 2 (64)	49 ± 1 (7)	0.11:1:5.82	60.6 ± 0.01	85 ± 1 (0.5)
	NIP	92 ± 2 (382)	88 ± 4 (73)		1:5.24	63.3 ± 0.01	93 ± 1 (0.2)
TM8	MIP _{CAF}	93 ± 1 (387)	87 ± 1 (72)	64 ± 1 (7)	0.09:1:5.36	62.3 ± 0.01	75 ± 1 (0.8)
	MIP _{THP}	93 ± 2 (386)	82 ± 1 (69)	77 ± 1 (8)	0.12:1:5.63	61.0 ± 0.01	98 ± 2 (0.3)
	NIP	86 ± 2 (360)	79 ± 1 (65)		1:5.57	68.7 ± 0.01	89 ± 1 (0.5)
MX10	MIP _{CAF}	88 ± 1 (409)	70 ± 1 (32)	35 ± 1 (4)	0.08:1:12.60	63.8 ± 0.1	117 ± 1 (0.2)
	MIP _{THP}	86 ± 2 (392)	61 ± 1 (28)	32 ± 1 (4)	0.13:1:14.15	75.7 ± 0.1	114 ± 1 (0.2)
	NIP	86 ± 2 (390)	79 ± 2 (36)		1:10.89	63.3 ± 0.1	128 ± 1 (0.5)

¹T:fM:X = template : functional monomer : cross-linker (mol) ratio in the polymers, ²Degree of cross-linking compared to the initial ratio -C=C- and -C=O- and in the polymers. ³ Polymers produced using T:fM = 1:4, fM:X = 1:5 and I:tM of 1:100.

Table S1 (continuation). Imprinting results of polymers synthesized from various template:functional monomer (TM), functional monomer:cross-linker (MX) and initiator:total monomer (IM) ratios.

Experiments		Incorporated components in the polymers			Polymer Composition T :FM : XL ¹	Degree of Cross-linking ²	Hydro-dynamic size, d_H (PDI)
		% incorporation (μmol)					
		EGDMA	MAA	Template			
MX2	MIP _{CAF}	93 ± 2 (311)	78 ± 2 (130)	10 ± 2 (4)	0.03:1:2.41	49.6 ± 0.1	84 ± 1 (0.1)
	MIP _{THP}	93 ± 2 (310)	83 ± 2 (138)	31 ± 0 (13)	0.09:1:2.26	57.7 ± 0.1	67 ± 1 (0.1)
	NIP	93 ± 2 (366)	84 ± 1 (57)		1:2.21	59.1 ± 0.1	89 ± 1 (0.5)
IM5	MIP _{CAF}	98 ± 1 (410)	92 ± 2 (77)	26 ± 1 (12)	0.07:1:5.33	67.5 ± 0.01	136 ± 1 (0.2)
	MIP _{THP}	98 ± 1 (410)	93 ± 2 (77)	50 ± 1 (10)	0.13:1:5.33	68.4 ± 0.01	132 ± 1 (0.2)
	NIP	98 ± 1 (409)	88 ± 2 (73)		1:5.58	73.6 ± 0.06	122 ± 1 (0.3)
IM10	MIP _{CAF}	96 ± 1 (401)	84 ± 2 (70)	21 ± 1 (4)	0.06:1:5.75	72.2 ± 0.01	121 ± 1 (0.6)
	MIP _{THP}	96 ± 0 (398)	82 ± 1 (69)	52 ± 3 (11)	0.16:1:5.81	73.1 ± 0.01	102 ± 1 (0.6)
	NIP	97 ± 1 (404)	83 ± 1 (69)		1:5.83	69.4 ± 0.01	83 ± 2 (1.0)
IM500	MIP _{CAF}	64 ± 2 (266)	56 ± 0 (47)	16 ± 1 (3)	0.10:1:5.37	67.3 ± 0.01	104 ± 1 (0.3)
	MIP _{THP}	61 ± 2 (256)	57 ± 2 (48)	22 ± 0 (5)	0.07:1:5.69	65.2 ± 0.01	94 ± 1 (0.3)
	NIP	88 ± 2 (366)	69 ± 1 (57)		1:6.41	67.3 ± 0.01	140 ± 1 (0.3)
IM1000	MIP _{CAF}	40 ± 0 (165)	39 ± 2 (32)	8 ± 1 (2)	0.05:1:5.16	66.6 ± 0.01	107 ± 1 (0.3)
	MIP _{THP}	43 ± 2 (179)	38 ± 2 (32)	12 ± 1 (3)	0.08:1:5.64	67.4 ± 0.01	90 ± 1 (0.3)
	NIP	75 ± 3 (314)	39 ± 2 (32)		1:9.70	62.3 ± 0.01	119 ± 1 (0.3)

¹T:fM:X = template : functional monomer : cross-linker (mol) ratio in the polymers, ²Degree of cross-linking compared to the initial ratio -C=C- and -C=O- and in the polymers. ³Polymers produced using T:fM = 1:4, fM:X = 1:5 and I:tM of 1:100.

Table S2. Polymer feed composition of the systems investigated from various template:functional monomer (TM), functional monomer:cross-linker (MX) and initiator:total monomer (IM) ratios.

EXPT/Polymers	[template] (μmol)	[FM] (μmol)	[XL] (μmol)	[initiator] (μmol)	Volume of porogen (mL)	T:FM:XL	I:TM
IM1000				0.50			1:1000
IM500				1.0			1:500
IM100, MX5, TM4	20.80	83.33	416.67	5.00		1:4:20	1:100
IM10				50.00			1:10
IM5				100.00	5.00		1:5
MX2	42.00	167.00	333.00			1:4:8	
MX10	14.00	45.00	455.00			1:40:40	
TM2	42.00			5.00		1:2:10	1:100
TM6	21.00	83.00	416.67			1:4:20	
TM8	10.00					1:8:40	

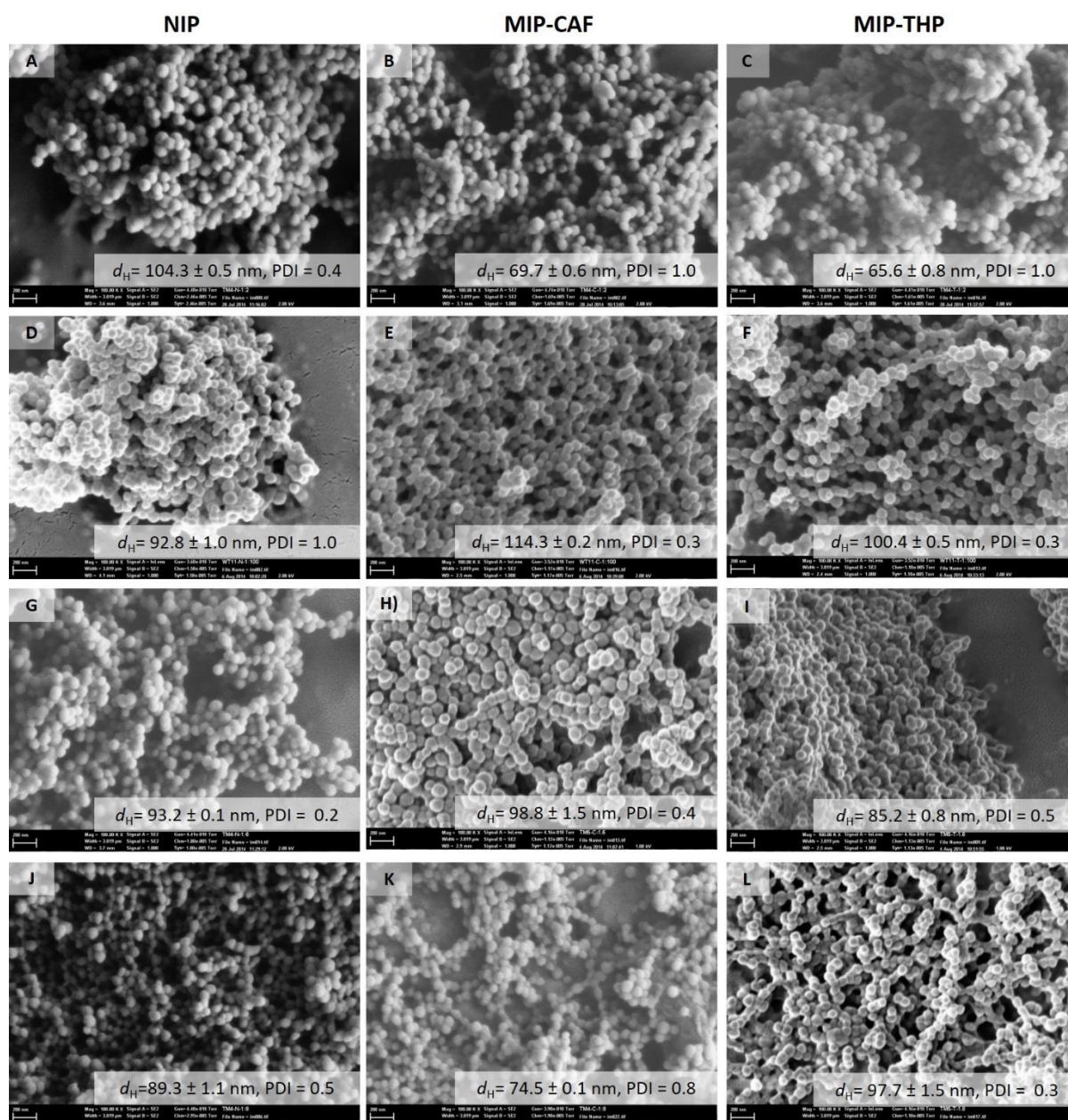


Figure S1. SEM images of microspheres synthesized from various template: functional monomer (T:fM) ratios: (A) TM2_{NIP}, (B) TM2_{CAF}, (C) TM2_{THP}, (D) TM4_{NIP}, (E) TM4_{CAF}, (F) TM4_{THP}, (G) TM6_{NIP}, (H) TM6_{CAF}, (I) TM6_{THP}, (J) TM8_{NIP}, (K) TM8_{CAF} and (L) TM8_{THP}. Scale bar represents 200 μ m at 100000x magnification. Insets are the hydrodynamic size of the microspheres with the corresponding polydispersity indexes (PDI) measured by DLS.

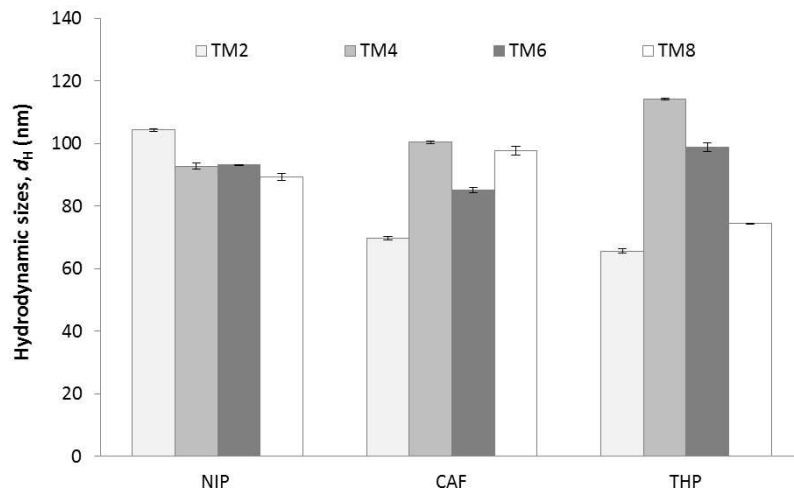


Figure S2. Hydrodynamic sizes, d_H , of microspheres synthesized from various T:fM ratios. Measurements were conducted using Dynamic Light scattering (DLS) and acetonitrile as the dispersant.

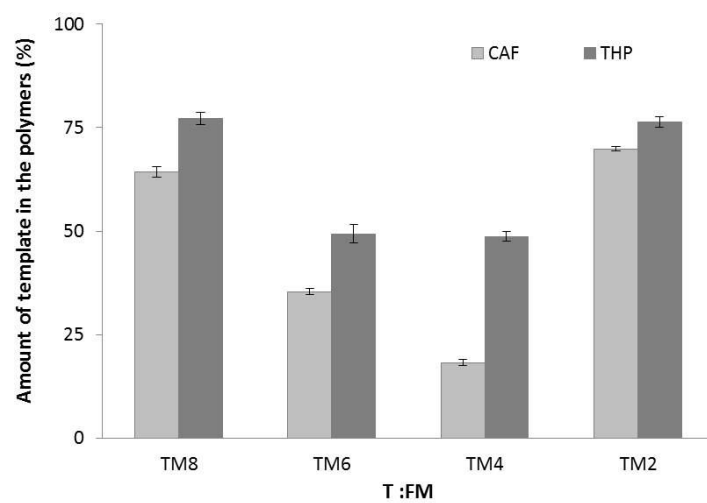


Figure S3. CAF and THP incorporated in the polymers from various T:fM ratios measured by ^1H NMR using 1,4-dioxane in $\text{DMSO-}d_6$ as the reference standard.

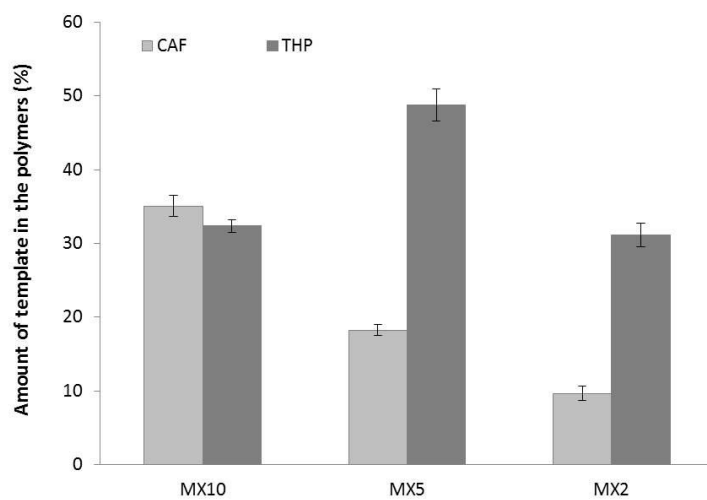


Figure S4. CAF and THP incorporated in the polymers from various fM:X ratios. Measured by ^1H NMR using 1,4-dioxane in $\text{DMSO-}d_6$ as the reference standard.

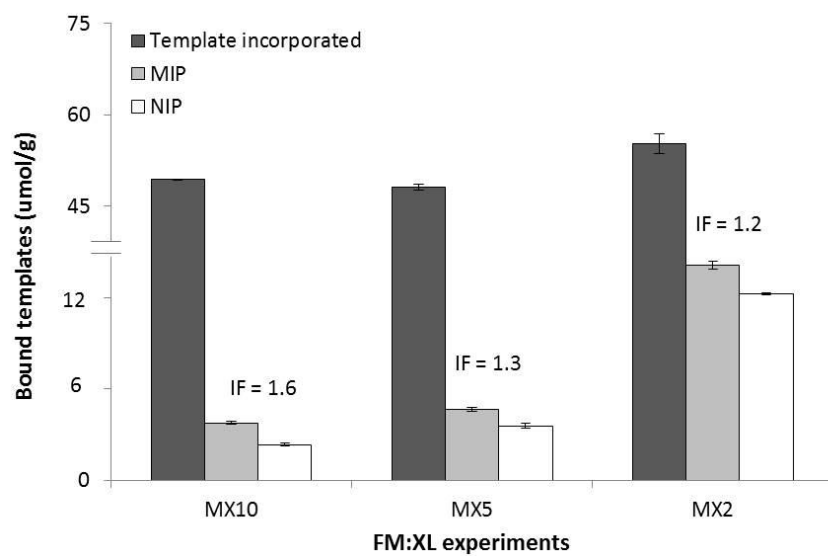


Figure S5. CAF incorporation and rebinding of MIPs and NIPs prepared from various fM:X ratios. Polymers were incubated for 18 hours in 100µM template rebinding solution and the post rebinding solutions were analyzed by HPLC.

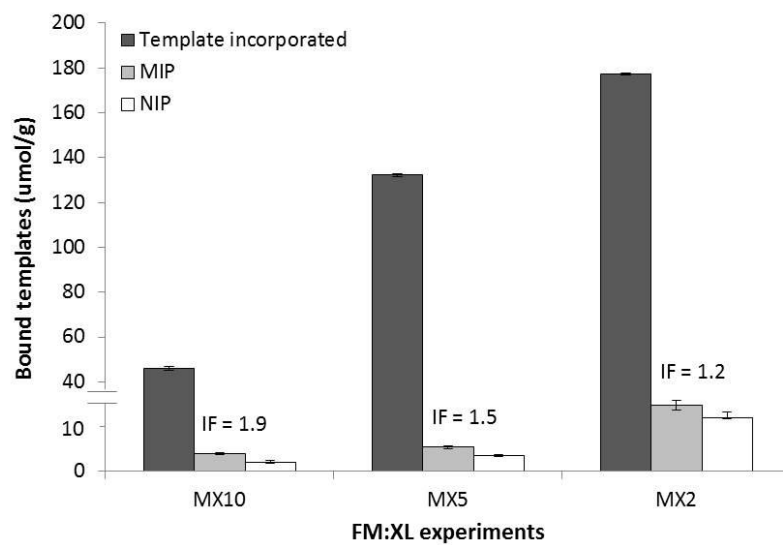


Figure S6. THP incorporation and rebinding of MIPs and NIPs prepared from various fM:X ratios. Polymers were incubated for 18 hours in 100 μ M template rebinding solution and the post rebinding solutions were analysed by HPLC.

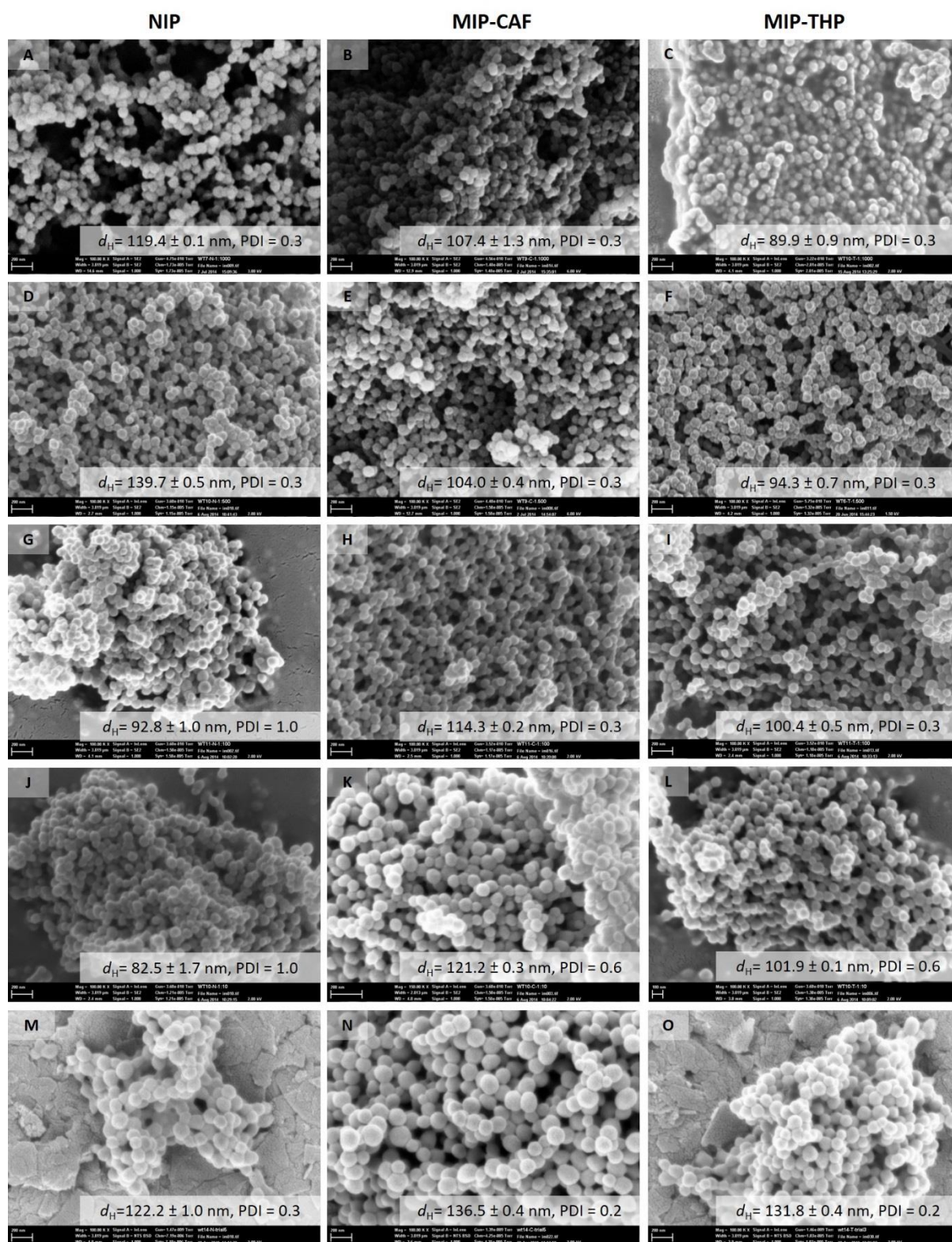


Figure S7. SEM images of microspheres synthesized from various initiator:total monomer (I:tM) ratios: (A) IM1000_{NIP}, (B) IM1000_{CAF}, (C) IM1000_{THP}, (D) IM500_{NIP}, (E) IM500_{CAF}, (F) IM500_{THP}, (G) IM100_{NIP}, (H) IM100_{CAF}, (I) IM100_{THP}, (J) IM10_{NIP}, (K) IM10_{CAF}, (L) IM10_{THP}, (M) IM5_{NIP}, (N) IM5_{CAF} and (O) IM5_{THP}. Scale bar represents 200 μ m at 100000x magnification. Insets are the hydrodynamic size of the microspheres with the corresponding polydispersity indexes (PDI) measured by DLS.

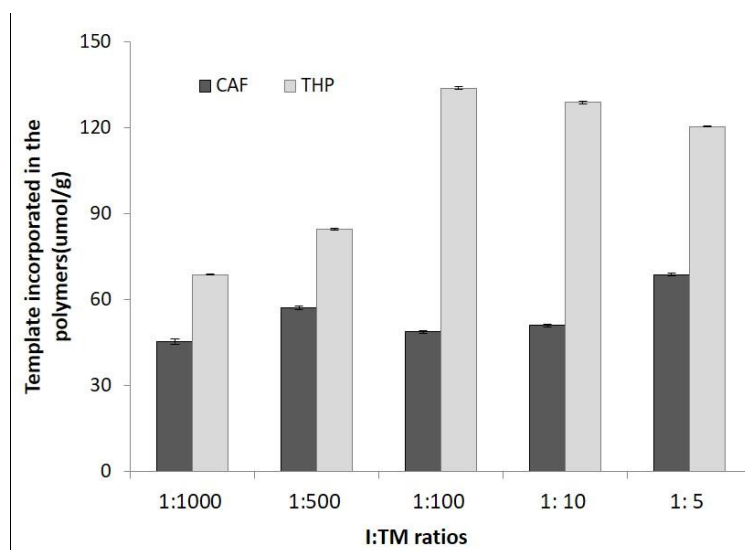


Figure S8. CAF and THP incorporation the polymers from various I:tM ratios measured by ^1H NMR using 1,4-dioxane in $\text{DMSO-}d_6$ as the reference standard.

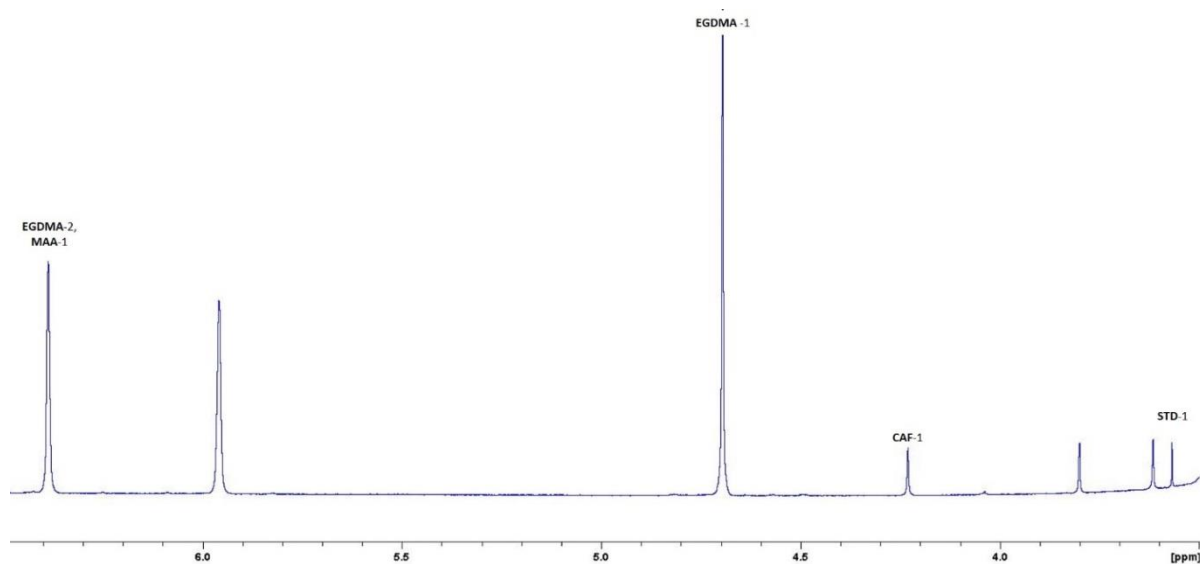


Figure S9. An example of a ^1H NMR spectrum of the caffeine pre-polymerization solution. Peaks of the components are as follows; cross-linker (EGDMA, O- CH_2 signal) at 4.32 ppm, functional monomer (the combination of the signals of $-\text{CH}_2=\text{CH}_2-$ of MAA and EGDMA) at 5.96 and 6.39 ppm and for caffeine at 4.23 ppm ($-\text{N}-\text{CH}_3$).