Electronic Supplementary Information (ESI) for

Polymer-Inorganic Hybrid Nanoparticles of Various Morphologies via Polymerization-Induced Self Assembly and Sol-Gel Chemistry

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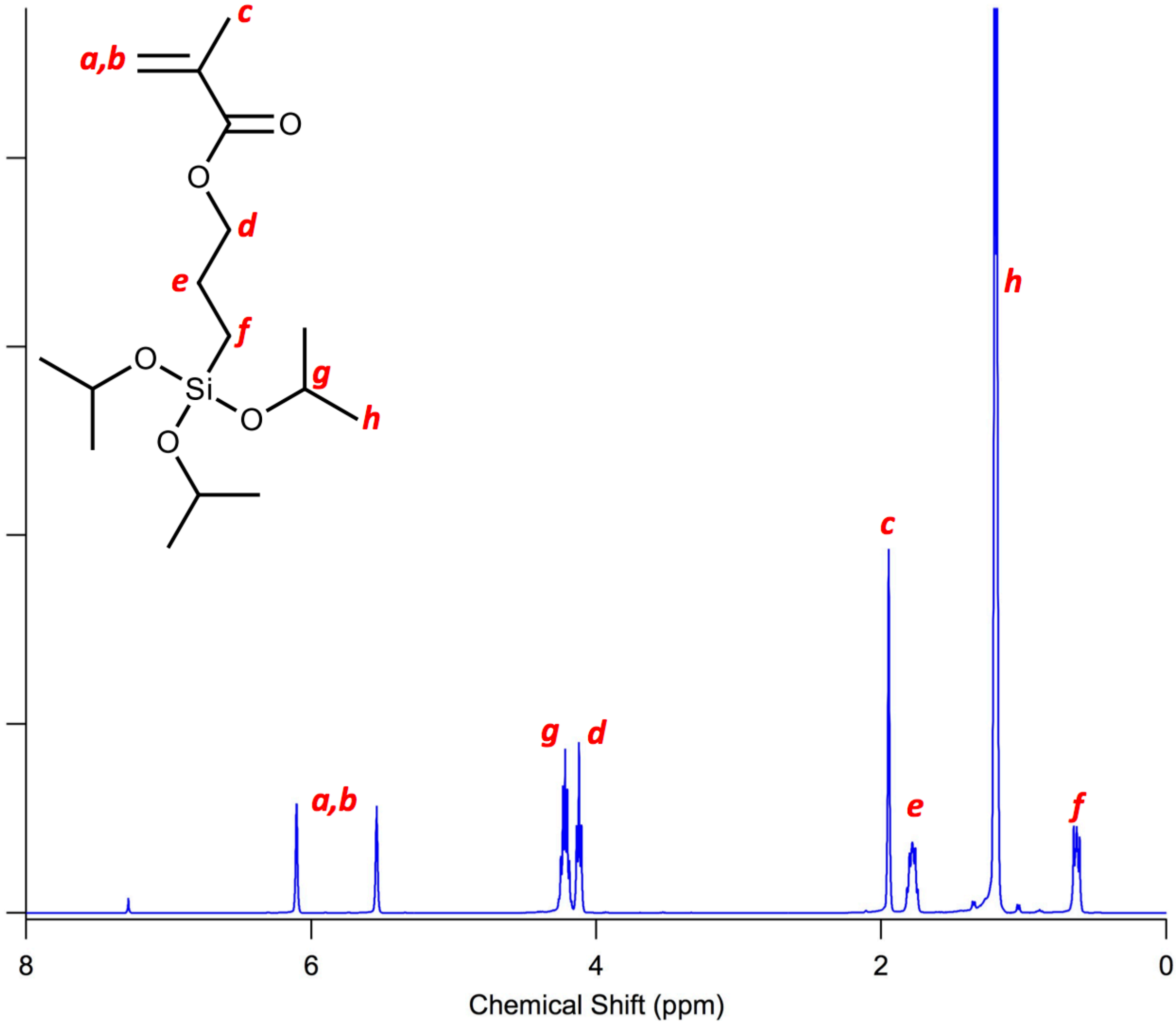


Figure S1. ^{1}H NMR spectrum (in $CDCl_3$) of IPS.

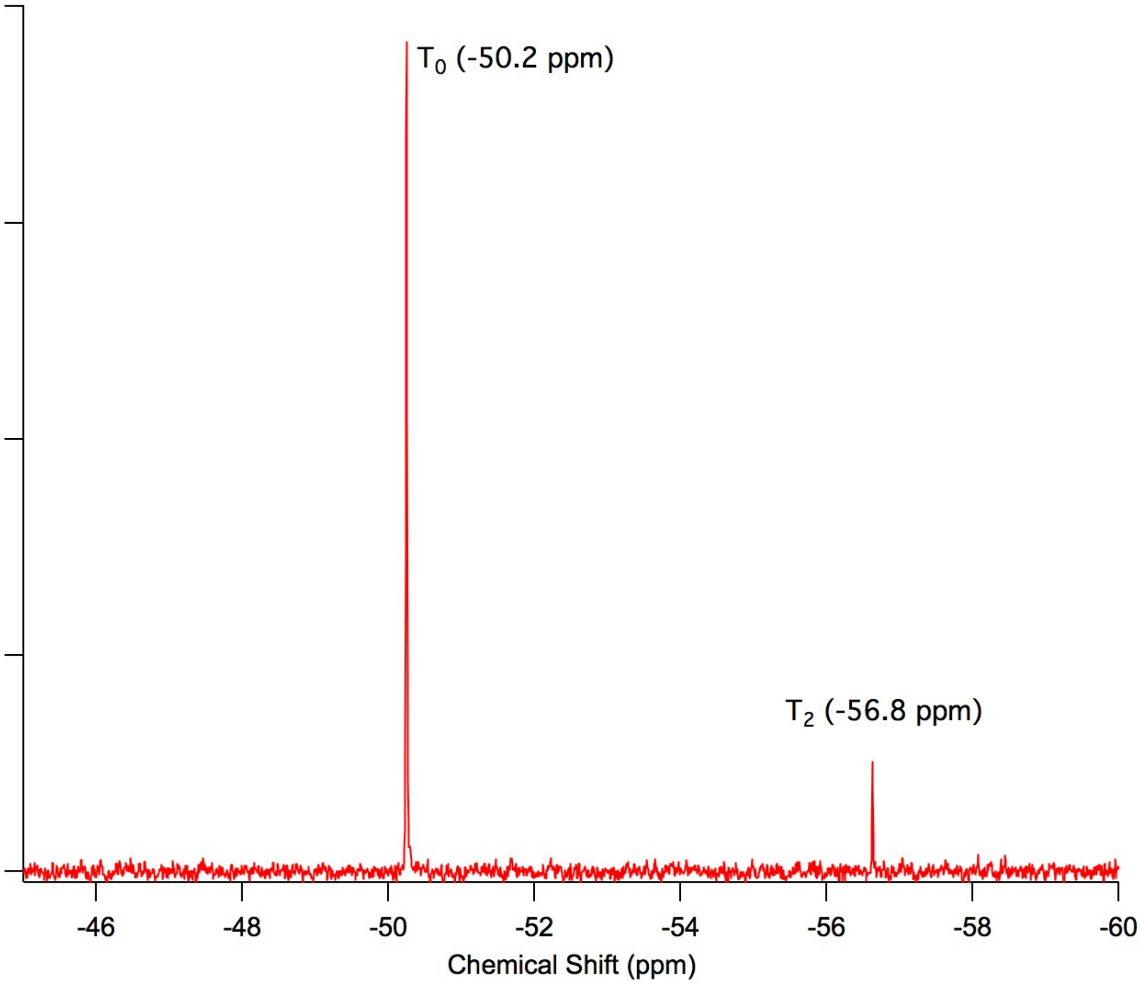


Figure S2. ^{29}Si NMR Spectra of IPS in $CDCl_3$.

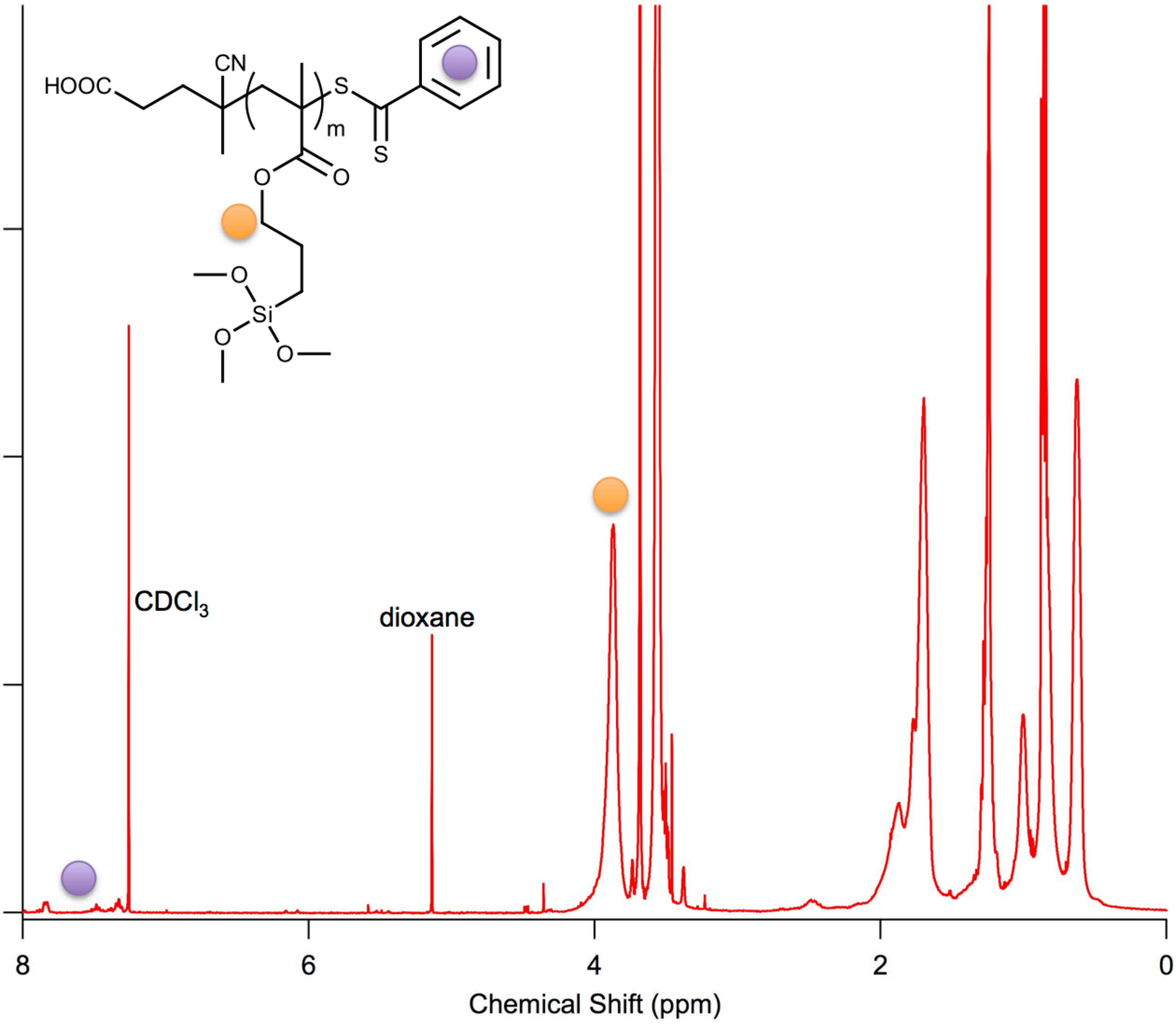


Figure S3. ^{1}H NMR of macroRAFT agent D-MPS$_{40}$ (Entry 2, Table 1 main text).

Table S1. XPS Analysis of macroRAFT agents.

Entry	**Sample Code**	**Conversion**	**DP_{th}**	**DP (^{1}H NMR)**	**Si, S content (at. %)**	**Si:S ratio**	**DP (XPS)**
Dithiobenzoate (CPADB) mediated macroRAFT synthesis							
1	D-MPS_{40}	0.98	39	41	7.25, 0.22	33	66
2	D-MPS_{65}	0.97	63	66	6.71, 0.15	45	90
3	D-IPS_{40}	0.97	39	48	6.85, 0.28	24.5	49
4	D-IPS_{65}	0.97	63	72	9.53, 0.25	38	76

The Si:S ratio was used to estimate the DP of our polymer chains, given that there is one Si atom per monomer repeat unit, and two S atoms per endgroup. This estimation is reliant on no loss of RAFT end-groups during synthesis or storage.

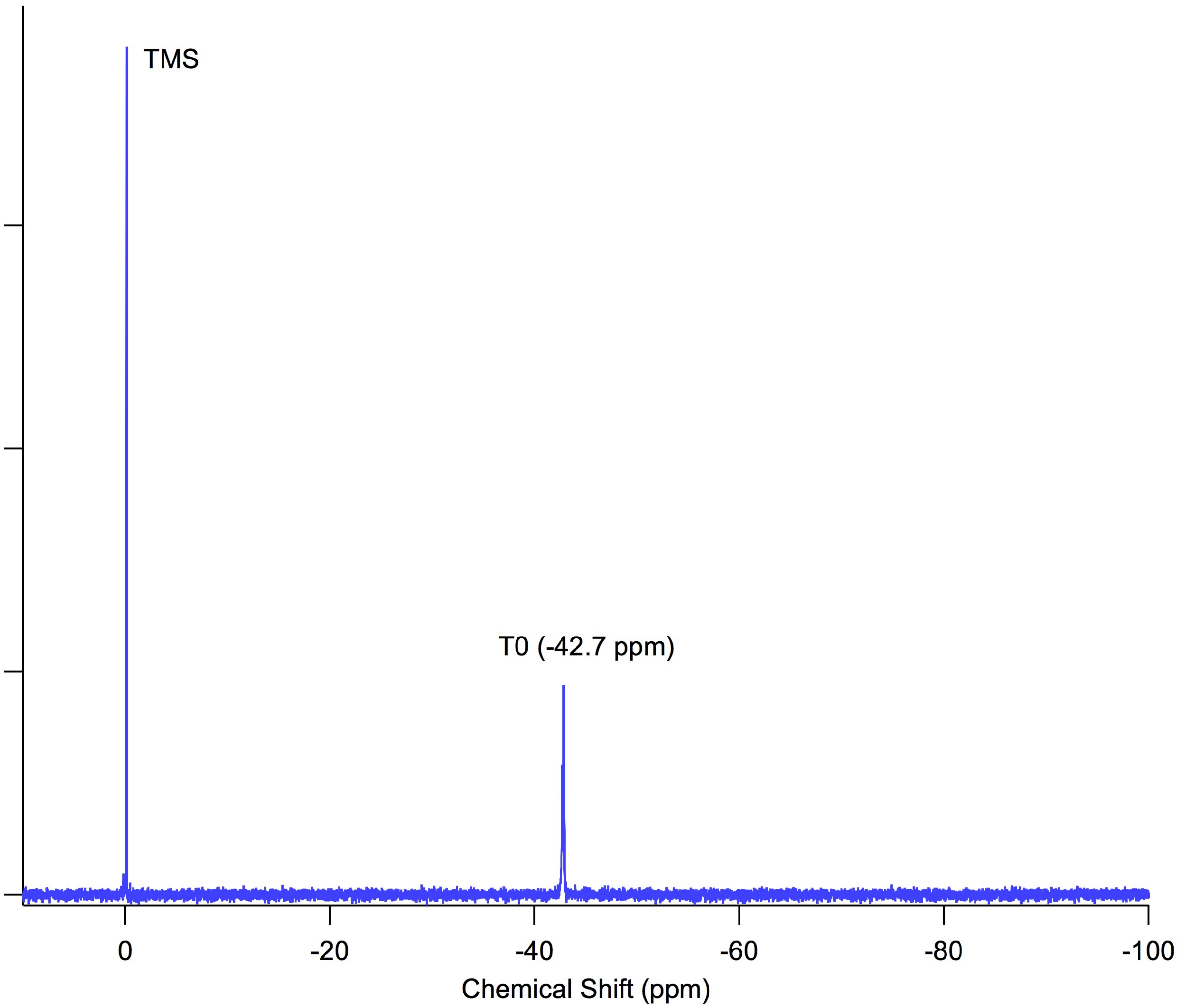


Figure S4. Solution-based ^{29}Si NMR Spectra of D-MPS$_{40}$ (CDCl$_3$ +TMS as internal reference)

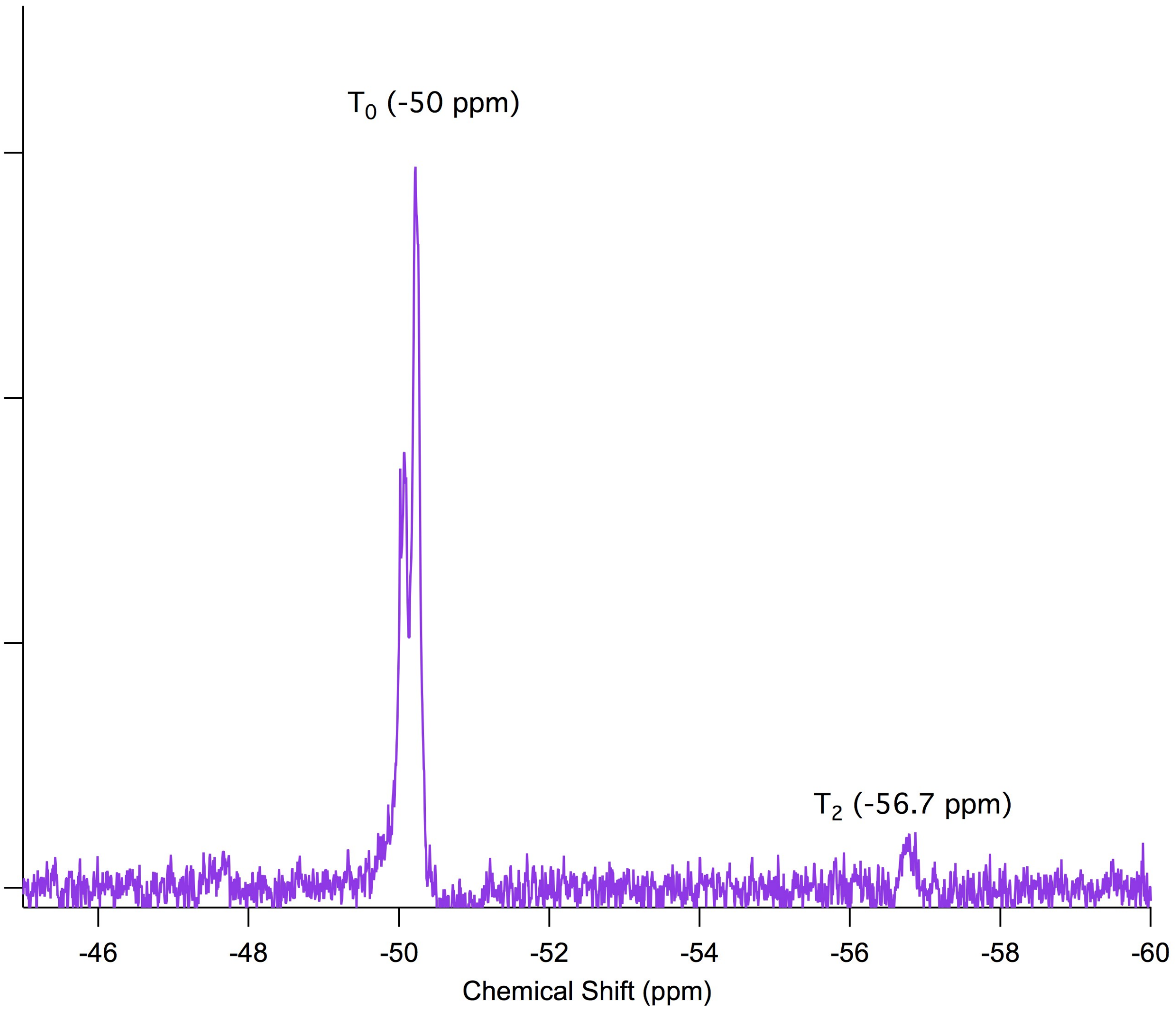


Figure S5. ^{29}Si NMR of D-IPS$_{40}$ after precipitation into methanol/water (8:2 v/v)

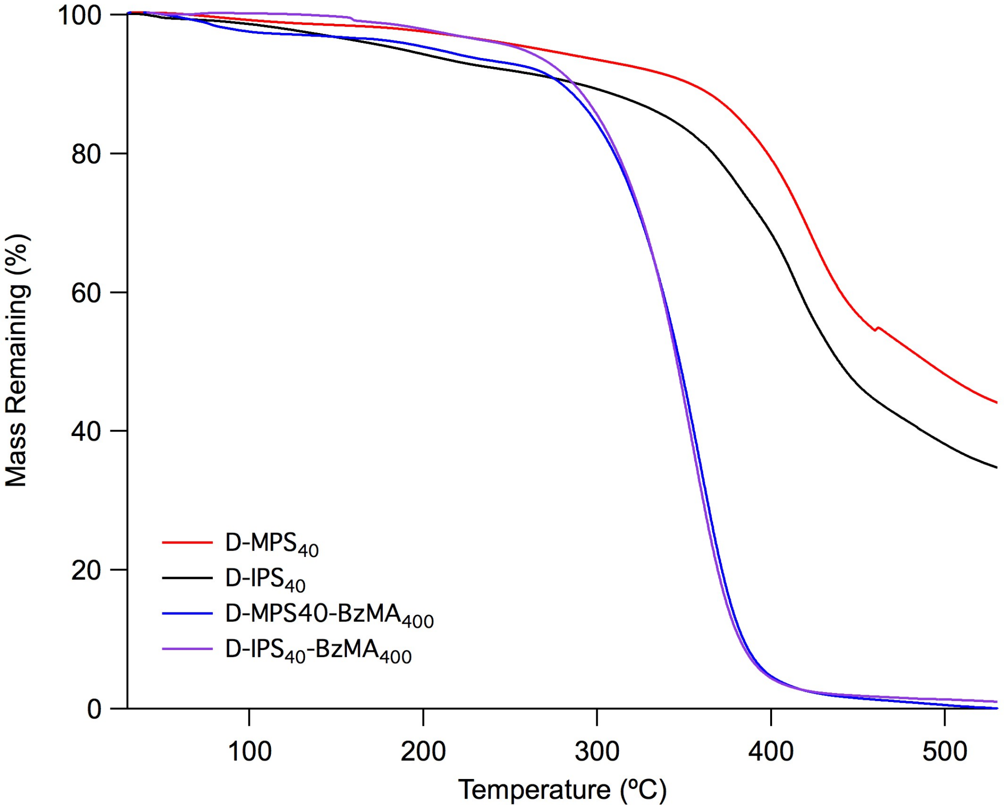


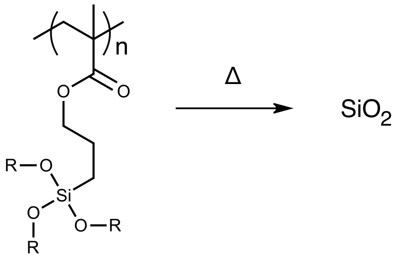
Figure S6. Thermogravimetric analysis of MPS and IPS macroRAFT agents (red and black curves) in addition to chain extension with 400 units of BzMA (blue and purple curves).

Table S2. Residual mass from TGA for different macroRAFT agents.

Entry	Sample Code	Residual Mass (%)
1	D-MPS$_{40}$	41.8
2	D-MPS$_{65}$	40.6
3	D-IPS$_{40}$	32.6
4	D-IPS$_{65}$	36.5

The predicted residual mass of our alkoxysilane macroRAFT agent precursors is estimated as follows:

- Effects due to polymer end-groups are neglected;
- The alkoxysilane group within the polymer backbone leads to the formation of silica upon elevated heating under TGA conditions which is left as residual at the conclusion of the measurement; all carbon, hydrogen (and additional oxygen) within the polymeric structure is lost via thermal decomposition.



For poly(MPS) and poly(IPS) respectively, the mass fraction of Si in the structure is:

MPS: % Si = 28/248 = 11.3 % (by mass)
IPS: % Si = 28/332 = 8.4 % (by mass)

Assuming all Si present converts to silica, the predicted residual mass is:

Residual mass (MPS): = 24.3 %
Residual mass (IPS): 18.1 %

This predicted residual mass represents a lower bound on the actual value, which is ~ 15 % greater. We postulate that a significant carbon content remains, potentially incorporated into the cross-linked residue.

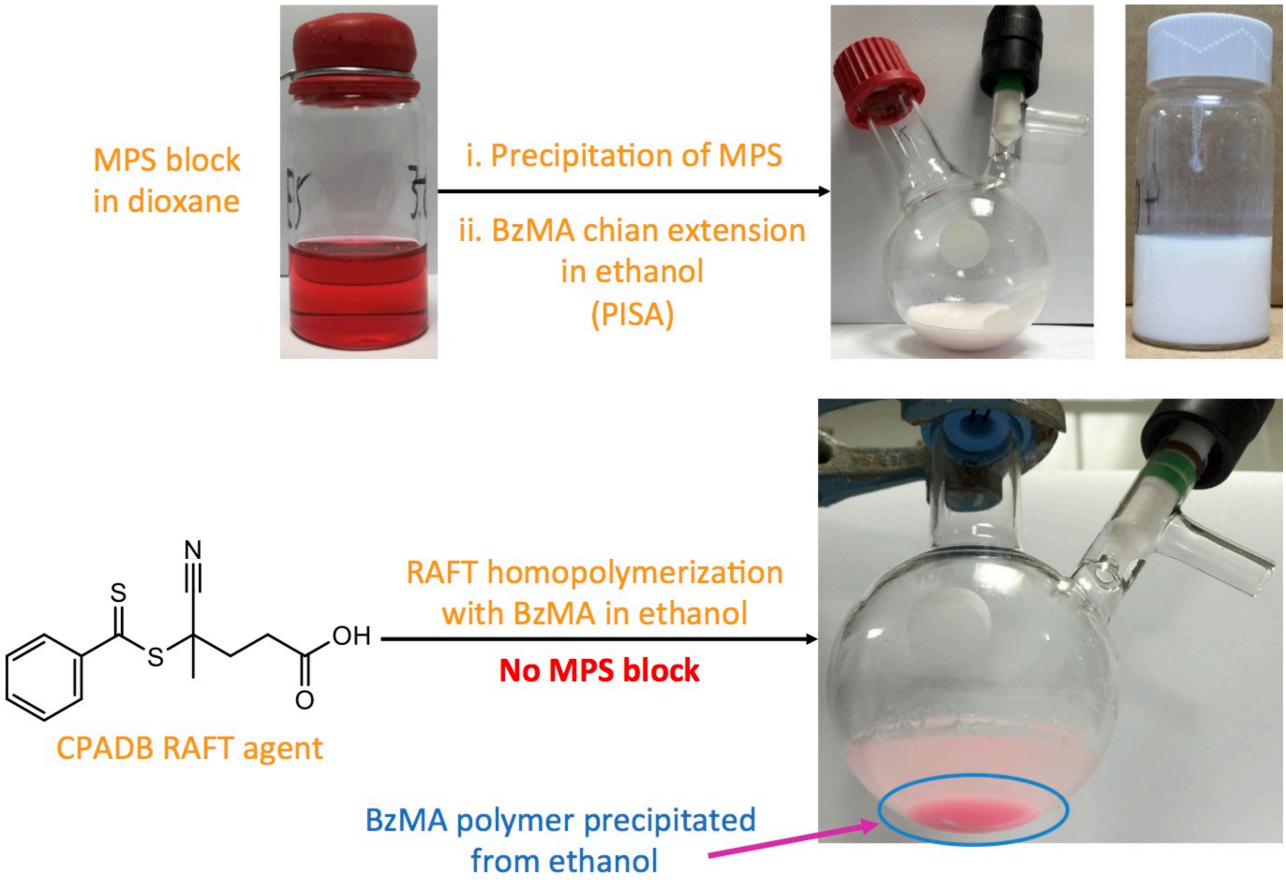


Figure S7. RAFT Polymerization of BzMA in ethanol. (Top): PISA process in the presence of a solvophilic poly(MPS) block; (Bottom): Absence of poly(MPS) block, showing polymer precipitation.

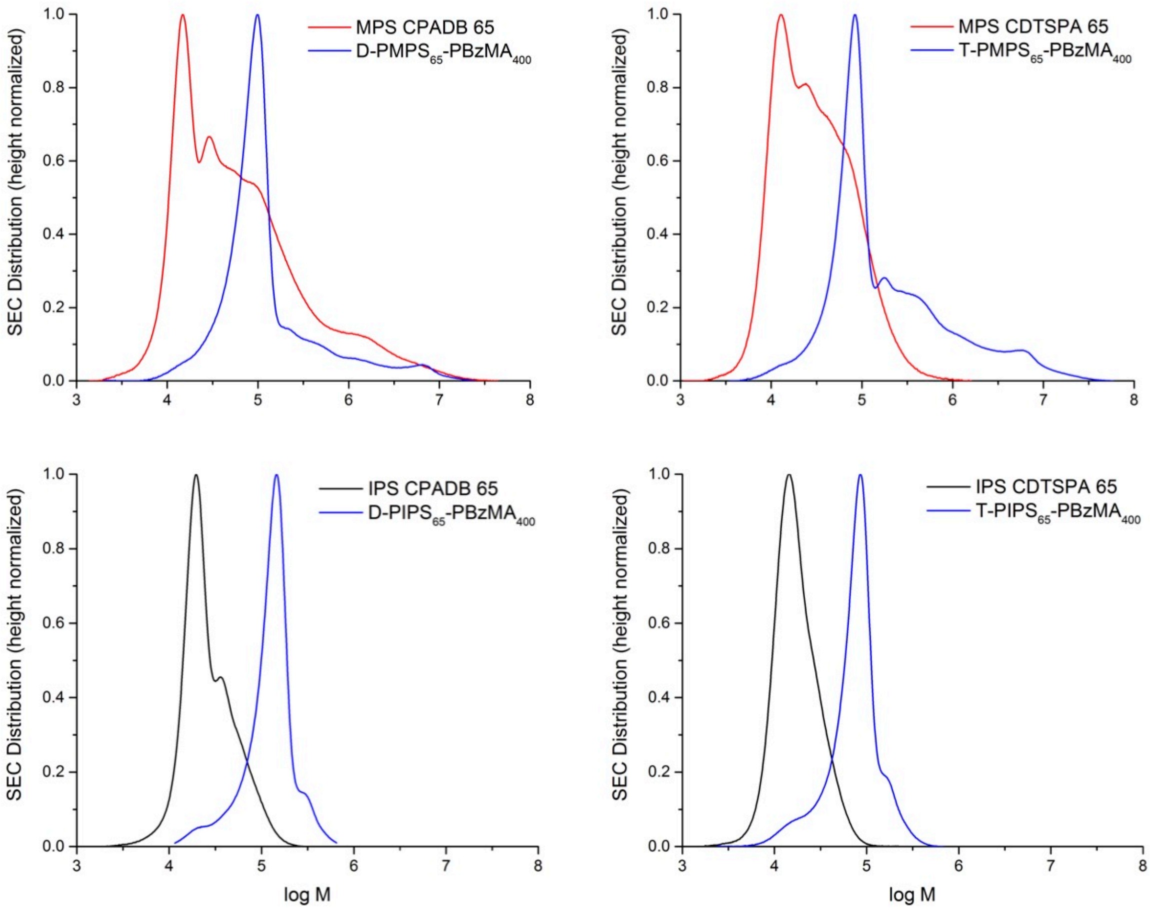


Figure S8. SEC distributions of the MPS- and IPS-based macroRAFT agents with 65 monomer repeat units in addition to subsequent chain extension with 400 units of benzyl methacrylate.

Table S3. MPS trithiocarbonate results

Entry	**Stabilizer**	**Target BzMA DP**	**BzMA conversion**	d_z **(nm)/PDI (DLS)**	**EM Observation**
37	T-MPS$_{40}$	100	0.99	231/0.22	Spheres, some vesicles
38		200	0.99	930/0.04	Vesicles
39		300	0.99	648/0.07	Vesicles
40		400	0.99	995/0.18	Vesicles
41	T-MPS$_{65}$	100	0.99	219/0.82	Rods, Ill-defined
42		200	0.99	150/0.18	Lumpy rods
43		300	0.99	570/0.55	Rods and spheres
44		400	0.91	475/0.66	Vesicles and spheres

Table S4. IPS trithiocarbonate results

Entry	**Stabilizer**	**Target BzMA DP**	**BzMA conversion**	d_z **(nm)/PDI (DLS)**	**EM Observation**
62 CT257’	T-IPS$_{40}$	400	0.98	129/0.06	Spheres
63 CT245		800	0.93	180/0.03	Spheres
64 CT321		1200	0.85	262/0.02	Spheres
65 CT322’		2500	0.99	447/0.05	Spheres
66 CT259	T-IPS$_{65}$	400	0.99	132/0.15	Spheres
67 CT319		1000	0.96	144/0.07	Spheres

Table S5. Number-average molecular weight and dispersity values for various macroRAFT agents after chain extension with 400 BzMA units.

Stabilizer	**Entry**	M_n **(SEC) (kDa)**	**Đ**
MPS	**23**	63.8	3.69
	36	68.1	5.12
	40	84.2	4.54
	44	76.0	8.27
IPS	**48**	68.9	1.62
	58	91.8	1.51
	62	57.2	1.36
	66	54.3	1.55

Predicted Size of Hybrid Polymer-Silica Particles After TEOS Growth

$$d_{pred} = d_{seed} \sqrt[3]{\frac{1.8x + 1.18}{1.8x}}$$

$$x = \frac{seed\ (g)}{silica\ (g)};\ silica(g) = \frac{m_{TEOS} \times 61}{208}$$

The density of the silica shell is assumed to be ~ 1.8 g/cm^3 and the density of the seed particle is assumed to be equivalent to the density of poly(benzyl methacrylate), which is 1.18 g/cm^3.

Reference: Tissot *et al., Macromolecules,* **2001,** 34, 5737.