Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

for

RAFT dispersion polymerization: A method to tune the morphologies of thymine-containing self-assembly

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1. Characterization data for all polymers

Table S1. Summary of characterization data of all polymers

Polymers	Solvent/mediator	Polyn time (hr)	Conv. (%)	$M_{n, th}$ (kDa)	$M_{n, NMR}$ (kDa)	$M_{n, SEC}$ (kDa) [a]	$Đ_M$
$PTMA_{40}$, **1**	1,4-dioxane	24	61	7.5	11.7	12.3	1.14
$PMMA_{70}$, **2**	toluene	5	36	4.5	6.8	7.0	1.17
$PMMA_{220}$, **3**	toluene	9	57	22.6	22.0	21.5	1.19
$PMMA_{70}$-*b*-$PTMA_{100}$, **4-100**	chloroform	24	97	36.1	45.1	42.8	2.88
$PMMA_{70}$-*b*-$PTMA_{100}$,**4-75**	chloroform:1,4-dioxane = 75:25	24	94	35.2	--	38.0	1.96
$PMMA_{70}$-*b*-$PTMA_{100}$, **4-50**	chloroform: 1,4-dioxane = 50:50	24	92	34.6	--	37.9	2.72
$PMMA_{70}$-*b*-$PTMA_{100}$, **4-33**	chloroform: 1,4-dioxane = 33:67	24	93	34.9	--	35.0	2.84
$PMMA_{70}$-*b*-$PTMA_{100}$, **4-25**	chloroform: 1,4-dioxane = 25:75	24	91	34.3	--	35.5	2.29
$PMMA_{70}$-*b*-$PTMA_{100}$, **4-12.5**	chloroform: 1,4-dioxane = 12.5:87.5	24	90	34.0	--	34.0	1.96
$PMMA_{70}$-*b*-$PTMA_{100}$, **4-0**	1,4-dioxane	24	87	33.1	--	30.0	1.44
$PMMA_{70}$-*b*-$PTMA_{20}$, **5**	chloroform	24	95	12.7	12.0	12.2	1.67
$PMMA_{70}$-*b*-$PTMA_{50}$, **6a**	chloroform	24	92	20.8	26.2	34.7	2.01
$PMMA_{70}$-*b*-$PTMA_{50}$, **6b**	1,4-dioxane	24	80	18.5	19.0	16.4	1.24
$PMMA_{70}$-*b*-$PTMA_{150}$, **7**	1,4-dioxane	24	95	49.8	--	40.1	1.84
$PMMA_{70}$-*b*-$PTMA_{200}$, **8**	1,4-dioxane	24	90	61.0	--	49.5	2.21
$PMMA_{70}$-*b*-$PTMA_{20}$, **5’**	chloroform + adenine -mediator	24	66	9.6	--	10.2	1.27
$PMMA_{70}$-*b*-$PTMA_{50}$, **6a’**	chloroform + adenine-mediator	24	87	20.1	--	22.2	2.19
$PMMA_{70}$-*b*-$PTMA_{100}$, **4-100’**	chloroform + adenine-mediator	24	95	35.5	--	33.5	3.10
$PMMA_{220}$-*b*-$PTMA_{50}$, **9a**	chloroform	24	91	35.5	34.4	34.3	1.72
$PMMA_{220}$-*b*-$PTMA_{50}$, **9b**	1,4-dioxane	48 24	85 61	34.1	35.7	30.1	1.17

[a] DMF eluent, PMMA as standards

2. Analysis of polymers 1-3

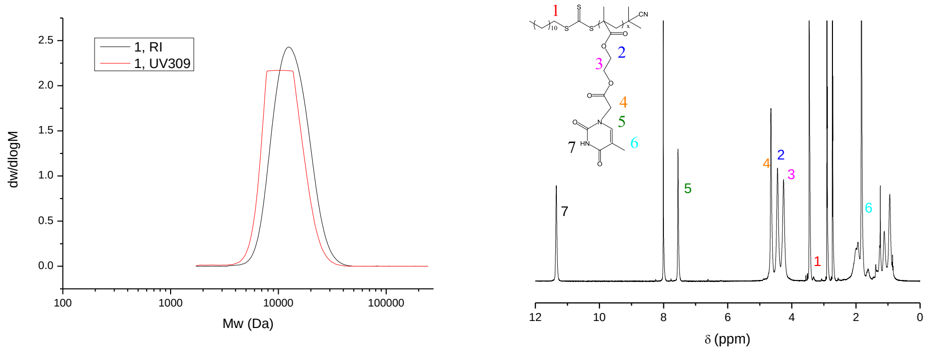


Figure S1. SEC analysis and ^{1}H NMR spectrum of homopolymer PTMA, **1** polymerized in 1,4-dioxane (DMF eluent, with PMMA standards).

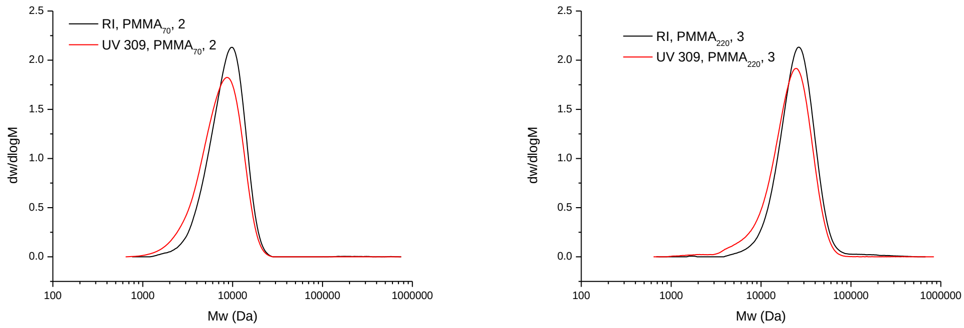
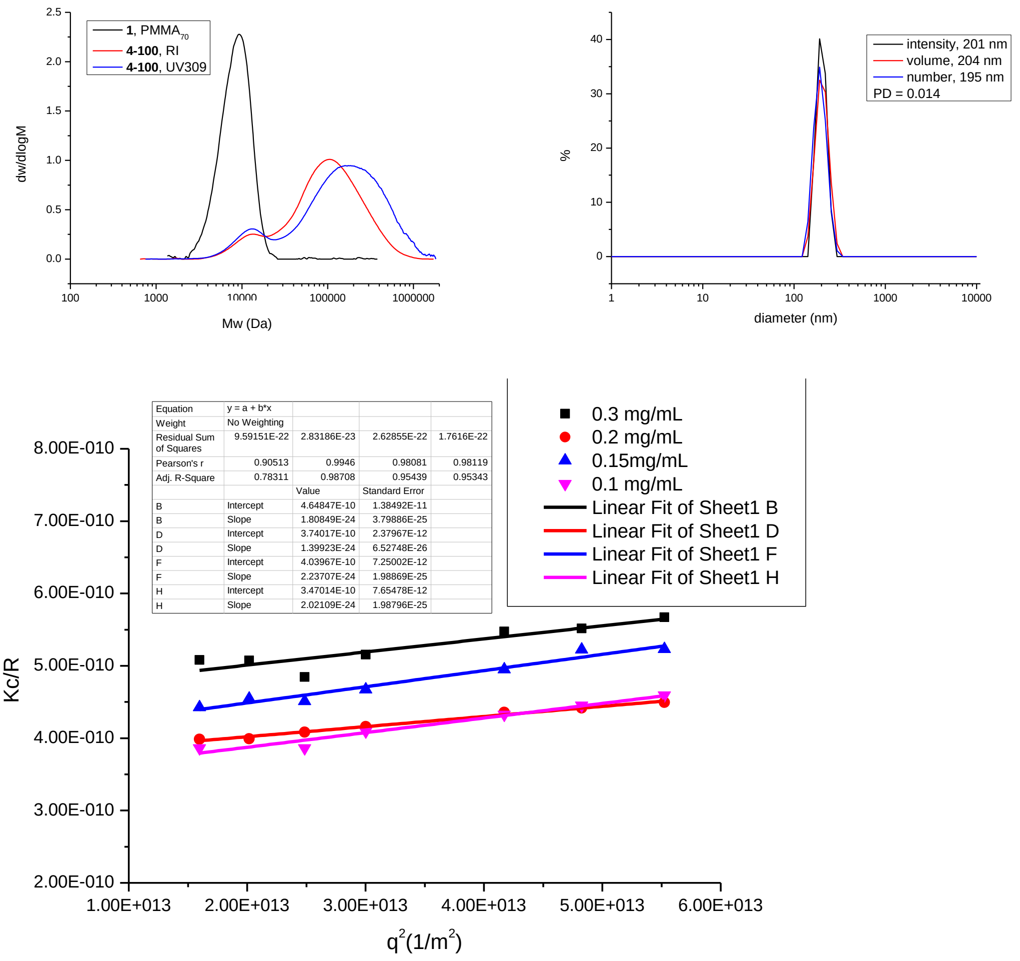


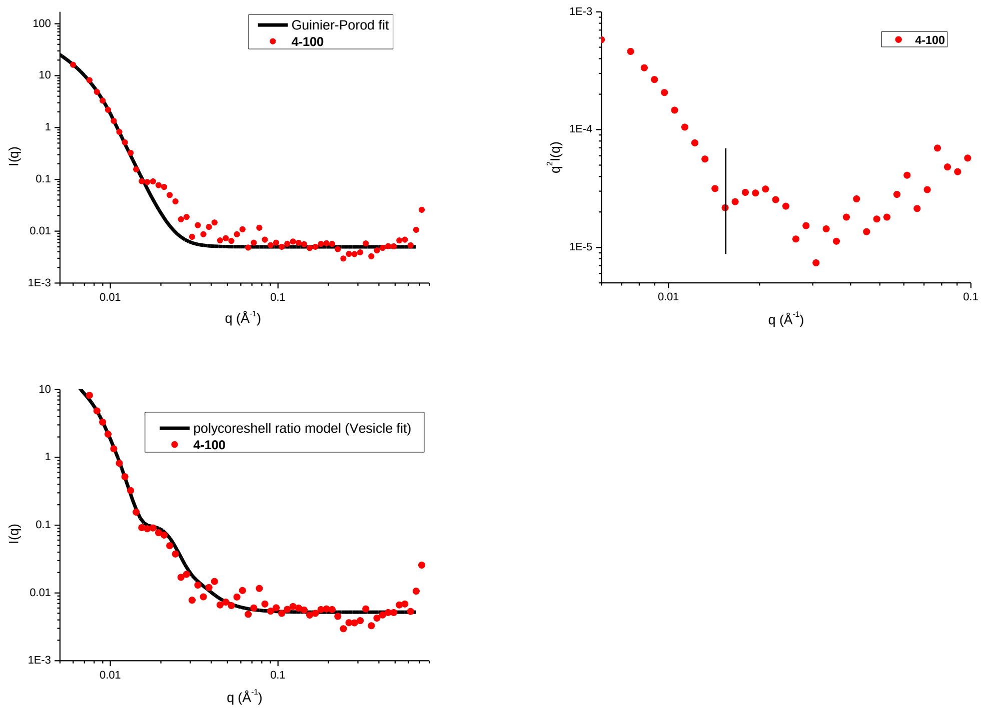
Figure S2. SEC analysis of PMMA macro-CTAs, **2** and **3** (DMF eluent, with PMMA standards).

3. Analysis of the assembly formed during polymerization in chloroform, 4-100



Equation	y = a + b*x			
Weight	No Weighting			
Residual Sum of Squares	9.59151E-22	2.83186E-23	2.62855E-22	1.7616E-22
Pearson's r	0.90513	0.9946	0.98081	0.98119
Adj. R-Square	0.78311	0.98708	0.95439	0.95343
		Value	Standard Error	
B	Intercept	4.64847E-10	1.38492E-11	
B	Slope	1.80849E-24	3.79886E-25	
D	Intercept	3.74017E-10	2.37967E-12	
D	Slope	1.39923E-24	6.52748E-26	
F	Intercept	4.03967E-10	7.25002E-12	
F	Slope	2.23707E-24	1.98869E-25	
H	Intercept	3.47014E-10	7.65478E-12	
H	Slope	2.02109E-24	1.98796E-25	

Figure S3. SEC analysis of **4-100** (DMF eluent, with PMMA standards), DLS distribution and Zimm plots (determined by SLS analysis) for the self-assemblies prepared during the polymerization, to afford PMMA$_{70}$-*b*-PTMA$_{100}$ in chloroform (**4-100**).



Data from Guinier-Porod fit:

Sample	R_g (nm)	s
4-100	25.6	0.70

s = 0: spheres; s = 1: rods; s = 2: platelets

Data from polycoreshell ratio model:

Core radius (nm)	Shell thickness (nm)	Total radius (nm)
70.0	38.3	108.3

The SLDs of the solvent and the core were fixed while the other parameters were left to float. Fittings with various manually inputted starting parameters were used to assess the validity of the fit.

Figure S4. SANS analysis of **4-100**, $PMMA_{70}$-*b*-$PTMA_{100}$ in deuterated chloroform: Experimental profile and Guinier-Porod fit (top left); plot to determine the thickness of the membrane (top right); experimental profile and polycoreshell ratio fit (bottom).

4. Analysis of the assembly formed during polymerization in chloroform and 1,4-dioxane mixtures, 4-75 to 4-12.5

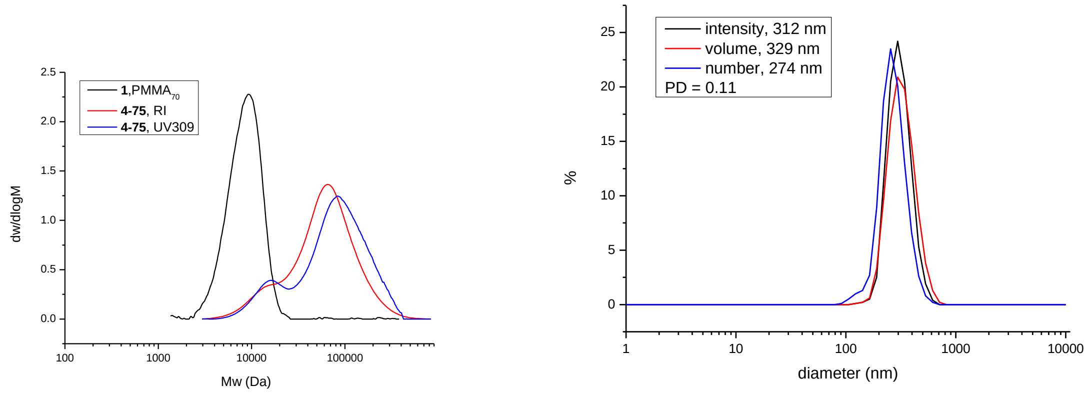


Figure S5. SEC analysis of **4-75** (DMF eluent, with PMMA standards) and DLS analysis of the self-assembly prepared from **4-75**, $PMMA_{70}$-*b*-$PTMA_{100}$ in a mixture of chloroform and 1,4-dioxane (v/v = 75:25).

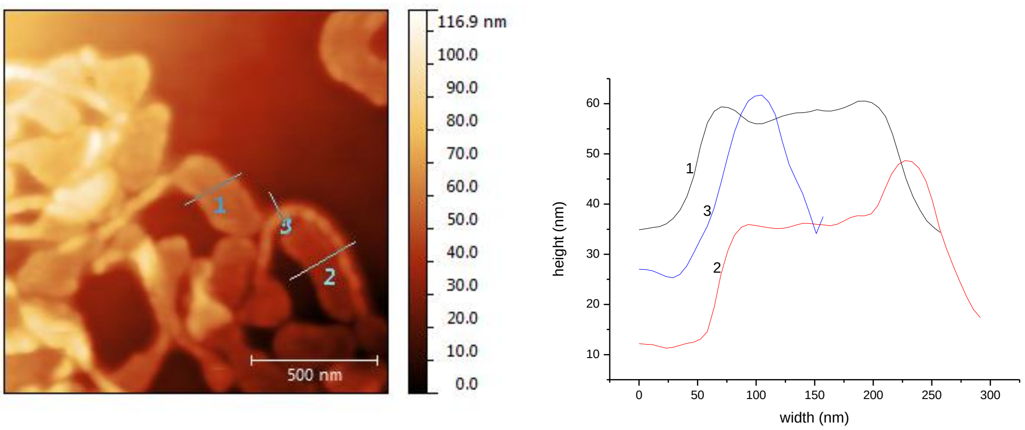


Figure S6. AFM height image of the self-assembly prepared in the polymerization **4-75**, $PMMA_{70}$-*b*-$PTMA_{100}$ in a mixture of chloroform and 1,4-dioxane (75:25, v/v) and the corresponding height profile.

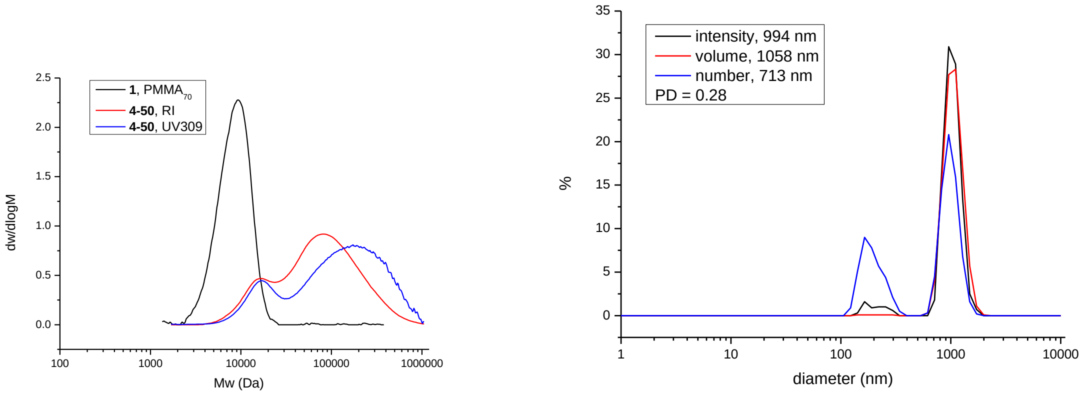


Figure S7. SEC analysis of **4-50** (DMF eluent, with PMMA standards) and DLS analysis of the self-assembly prepared from **4-50**, $PMMA_{70}$-*b*-$PTMA_{100}$ in a mixture of chloroform and 1,4-dioxane (v/v = 50:50).

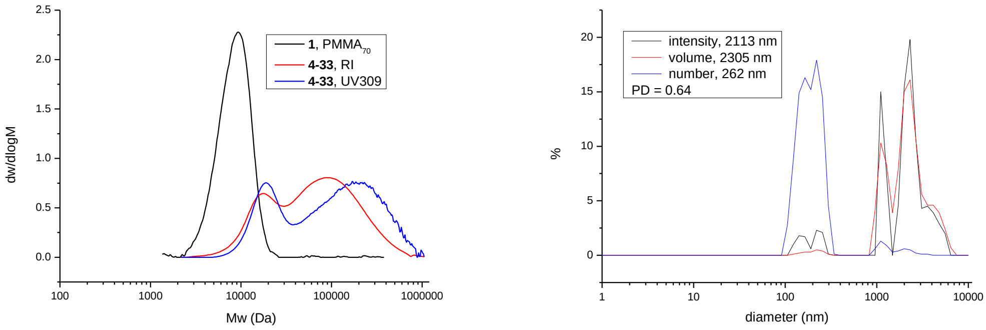


Figure S8. SEC analysis of **4-33** (DMF eluent, with PMMA standards) and DLS analysis of the self-assembly prepared from **4-33**, $PMMA_{70}$-*b*-$PTMA_{100}$ in a mixture of chloroform and 1,4-dioxane (v/v = 33:67).

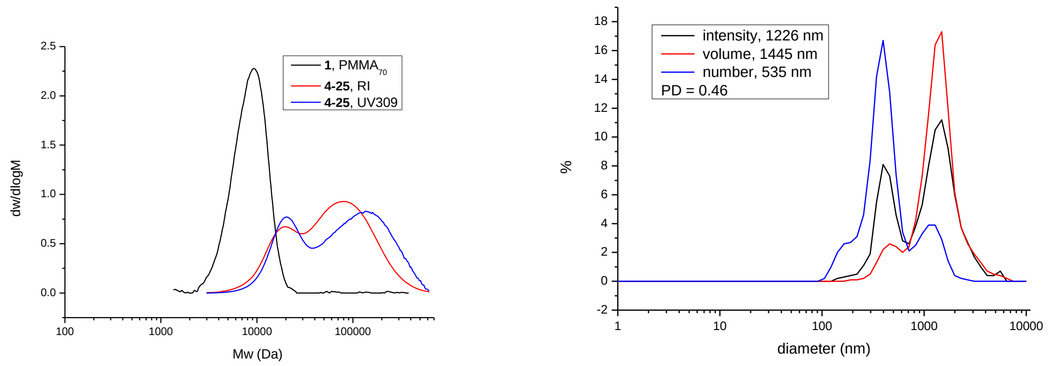


Figure S9. SEC analysis of **4-25** (DMF eluent, with PMMA standards) and DLS analysis of the self-assembly prepared from **4-25**, PMMA$_{70}$-*b*-PTMA$_{100}$ in a mixture of chloroform and 1,4-dioxane (v/v = 25:75).

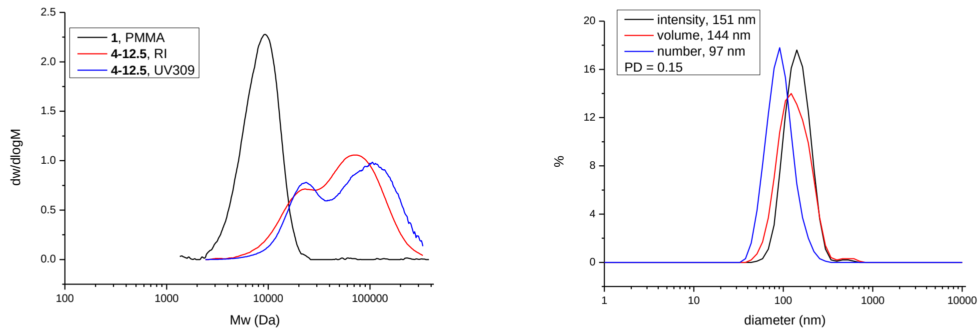


Figure S10. SEC analysis of **4-12.5** (DMF eluent, with PMMA standards) and DLS analysis of the self-assembly prepared from **4-12.5**, PMMA$_{70}$-*b*-PTMA$_{100}$ in a mixture of chloroform and 1,4-dioxane (v/v = 12.5:87.5).

5. Analysis of the assembly formed during polymerization in 1,4-dioxane, 4-0

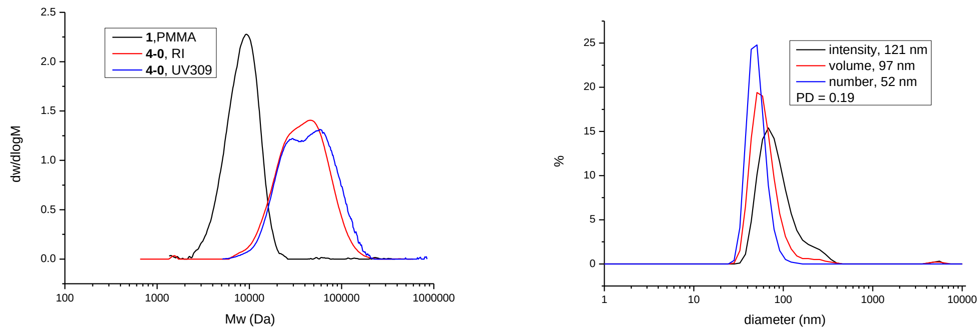


Figure S11. SEC analysis of **4-0** (DMF eluent, with PMMA standards) and DLS analysis of the self-assembly prepared from **4-0**, $PMMA_{70}$-*b*-$PTMA_{100}$ in 1,4-dioxane.

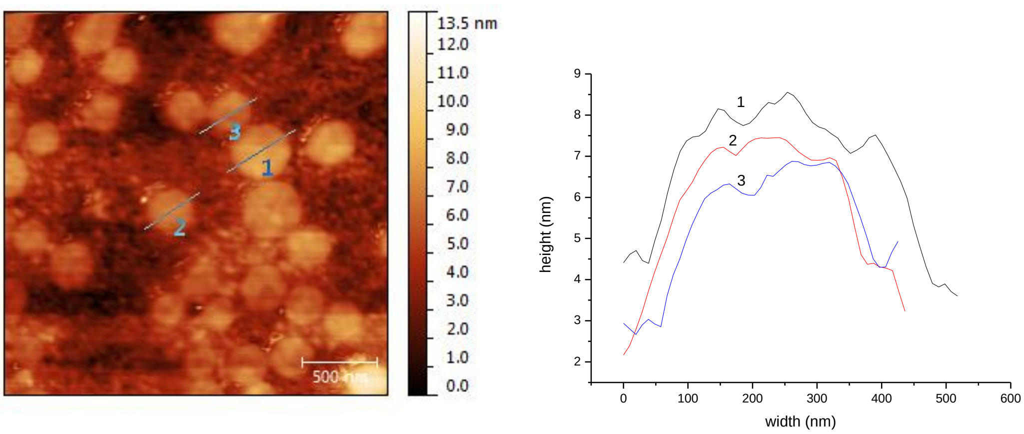


Figure S12. AFM height image of the self-assembly prepared in the polymerization **4-0**, $PMMA_{70}$-*b*-$PTMA_{100}$ in 1,4-dioxane and the corresponding height profile.

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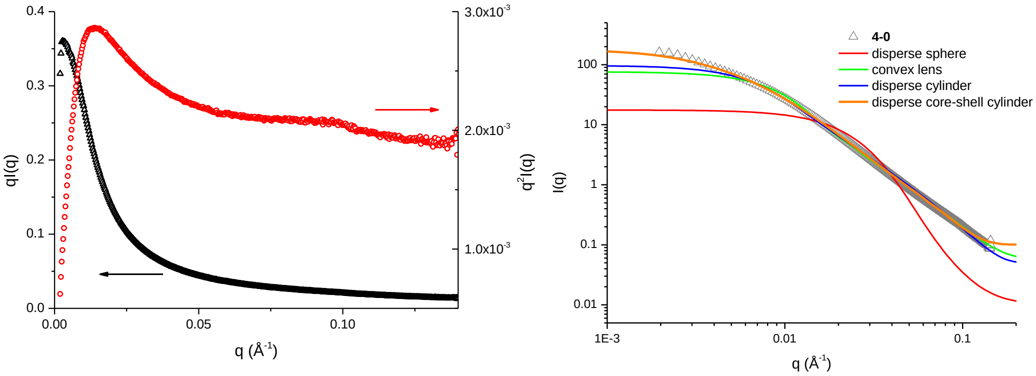


Model	disperse spheres	convex lens	disperse cylinder	core-shell cylinders
Radius core (nm)	4.9	29.3	21.6	8.8
Dispersity	0.4	-	0.3	0.7
Radius shell (nm)	-	-	-	8.4
Length (nm)	-	-	2.8	3.4
End cap radius	-	273	-	-
X^2 (quality of the fit)	3285k	837k	530k	59k

Figure S13. SAXS analysis of **4-0**, $PMMA_{70}$-*b*-$PTMA_{100}$ in 1,4-dioxane. Kratky plots for spheres and cylinders (left); experimental profile and fits with different models: disperse spheres (PCR), convex lens (CL), disperse cylinder (CYPR), and core-shell cylinder (CSCYPR) (right).

6. SEC analysis of the polymers formed in the polymerization of PTMA from macro-CTA 1 in a mixture of chloroform and 1,4-dioxane

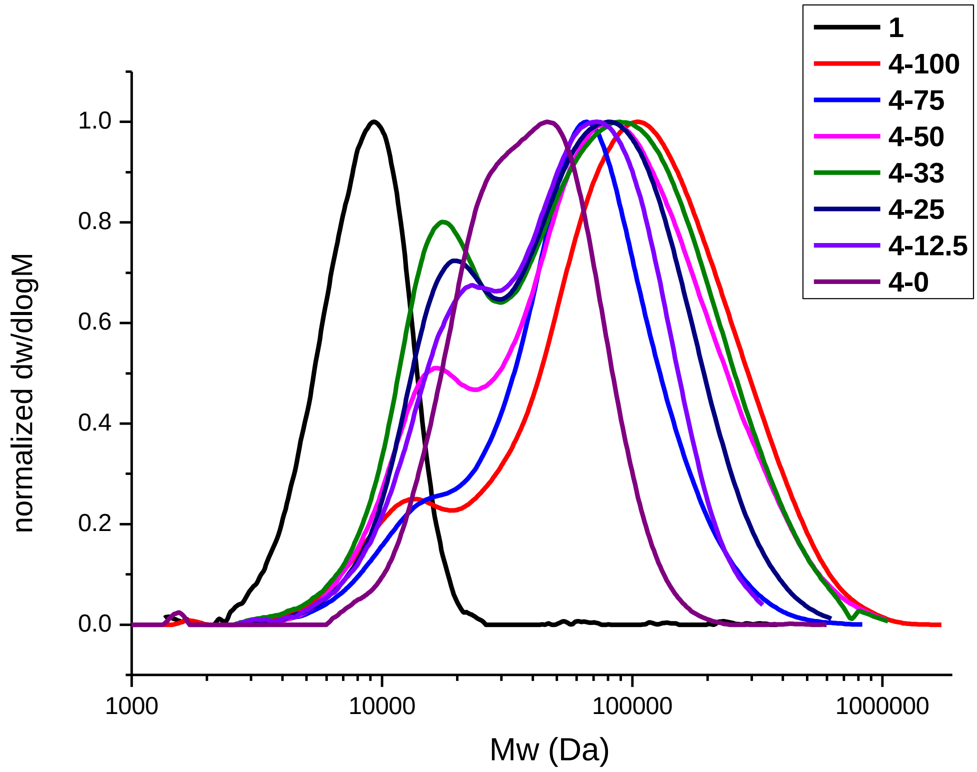


Figure S14. Normalized SEC traces of **2** and **4-X,** were **X** represents the volume ratio of chloroform in the polymerization solvent (DMF eluent, with PMMA standards).

7. Investigation into the stability of TMA in the presence of the CTA and heating

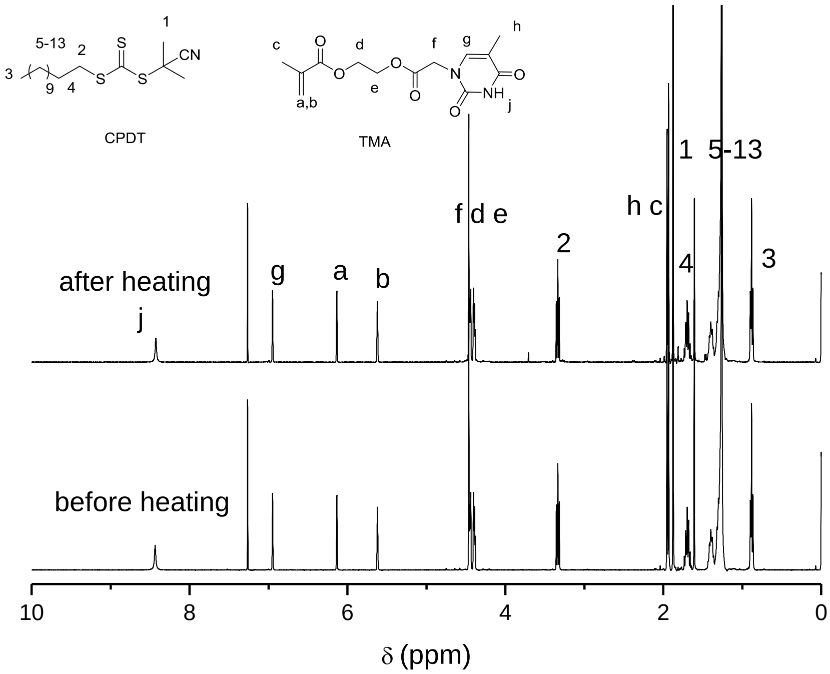
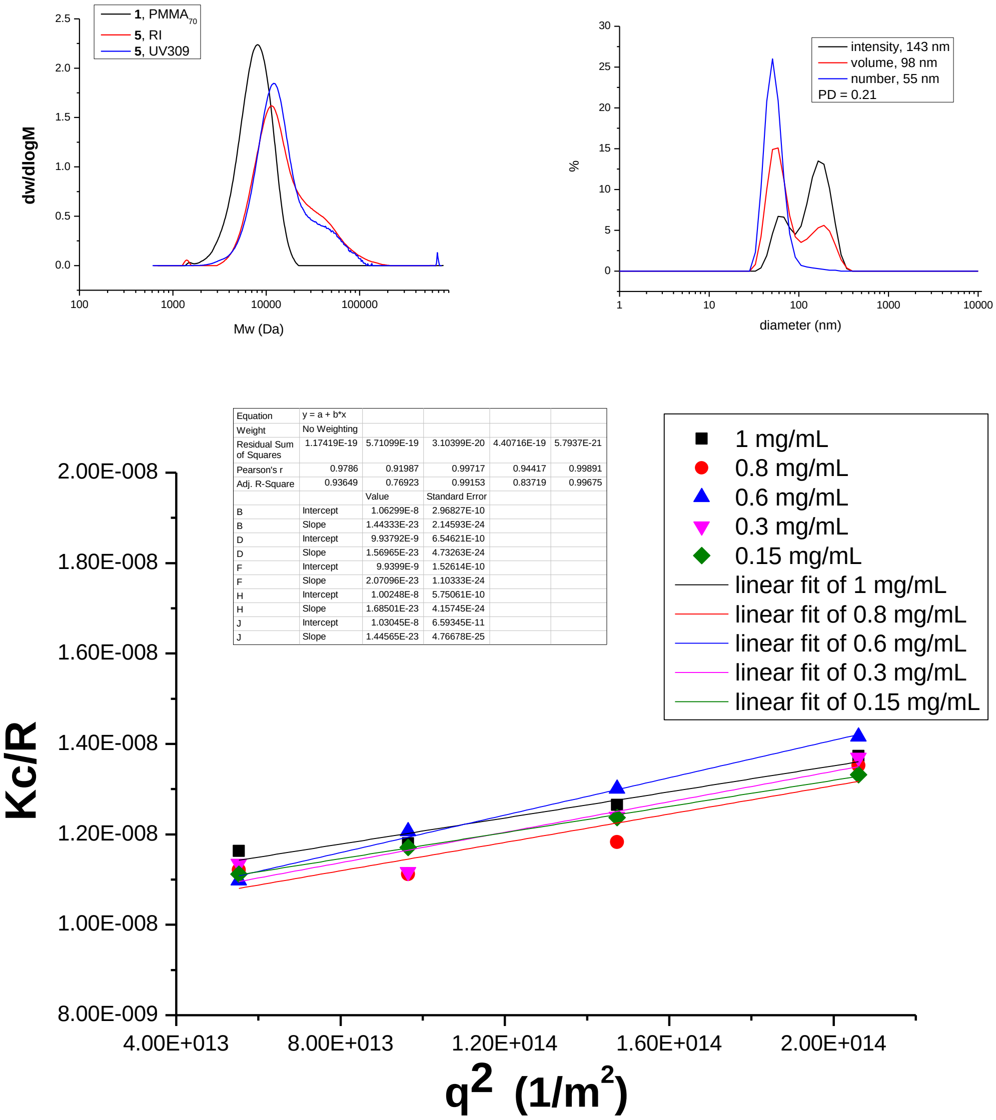


Figure S15. [1]H NMR spectra of a mixture of TMA and CTA (CPDT) in chloroform before and after heating for 24 hours.

8. Analysis of the polymers formed from macro-CTA 1 in chloroform



Equation	y = a + b*x				
Weight	No Weighting				
Residual Sum of Squares	1.17419E-19	5.71099E-19	3.10399E-20	4.40716E-19	5.7937E-21
Pearson's r	0.9786	0.91987	0.99717	0.94417	0.99891
Adj. R-Square	0.93649	0.76923	0.99153	0.83719	0.99675
		Value	Standard Error		
B	Intercept	1.06299E-8	2.96827E-10		
B	Slope	1.44333E-23	2.14593E-24		
D	Intercept	9.93792E-9	6.54621E-10		
D	Slope	1.56965E-23	4.73263E-24		
F	Intercept	9.9399E-9	1.52614E-10		
F	Slope	2.07096E-23	1.10333E-24		
H	Intercept	1.00248E-8	5.75061E-10		
H	Slope	1.68501E-23	4.15745E-24		
J	Intercept	1.03045E-8	6.59345E-11		
J	Slope	1.44565E-23	4.76678E-25		

Figure S16. SEC analysis of **5** (DMF eluent, with PMMA standards), DLS distribution and Zimm plots (determined by SLS analysis) for the self-assemblies prepared during the polymerization, to afford PMMA$_{70}$-*b*-PTMA$_{20}$ in chloroform.

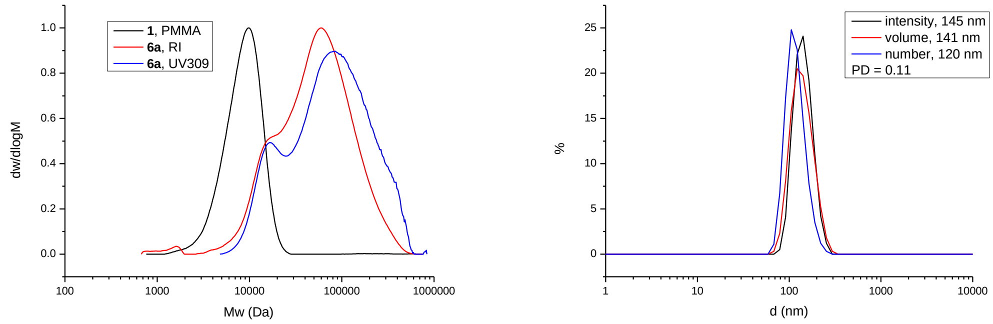
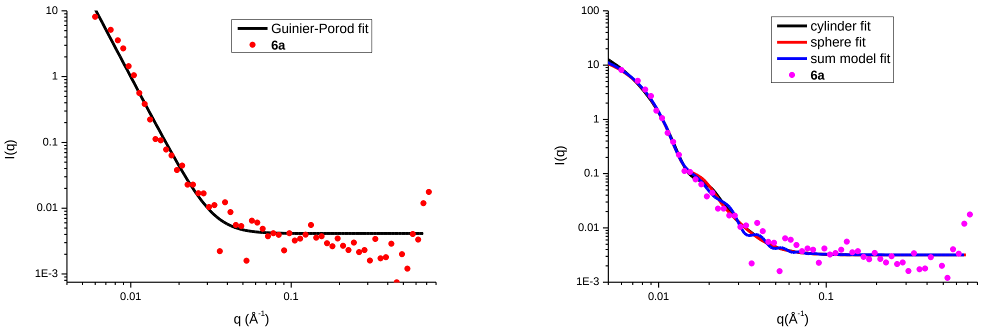


Figure S17. SEC analysis of **6a** (DMF eluent, with PMMA standards) and DLS analysis of the self-assembly prepared from **6a**, $PMMA_{70}$-*b*-$PTMA_{50}$ in chloroform.



Data obtained from Guinier-Porod fit:

Sample	R_g (nm)	s		Guinier fit (R_g, nm)*
6a	62.2	1.32	(high errors)	29.5

S = 0: spheres; s = 1: rods; s = 2: platelets

*The difference between the values of R_g is explained by the presence of elongated morphologies in solution. We suggest that the Guinier fit likely represents the cross-section of the elongated morphologies in solution and does not take into account their length. The R_g value given by the Guinier-Porod fit takes into account the length and cross-section of the extended morphologies, which explains the higher value obtained.

Data from sum of sphere model and cylinder model:

Cyl radius (nm)	Cyl length (nm)	Sphere radius (nm)
21.2	2484	32.3

Figure S18. SANS analysis of polymer **6a**, $PMMA_{70}$-*b*-$PTMA_{50}$ in chloroform. Experimental profile and Guinier-Porod fit (left); experimental profile and fits with sphere, cylinder and sum models (right).

9. Analysis of the polymers formed from macro-CTA 1 in 1,4-dioxane

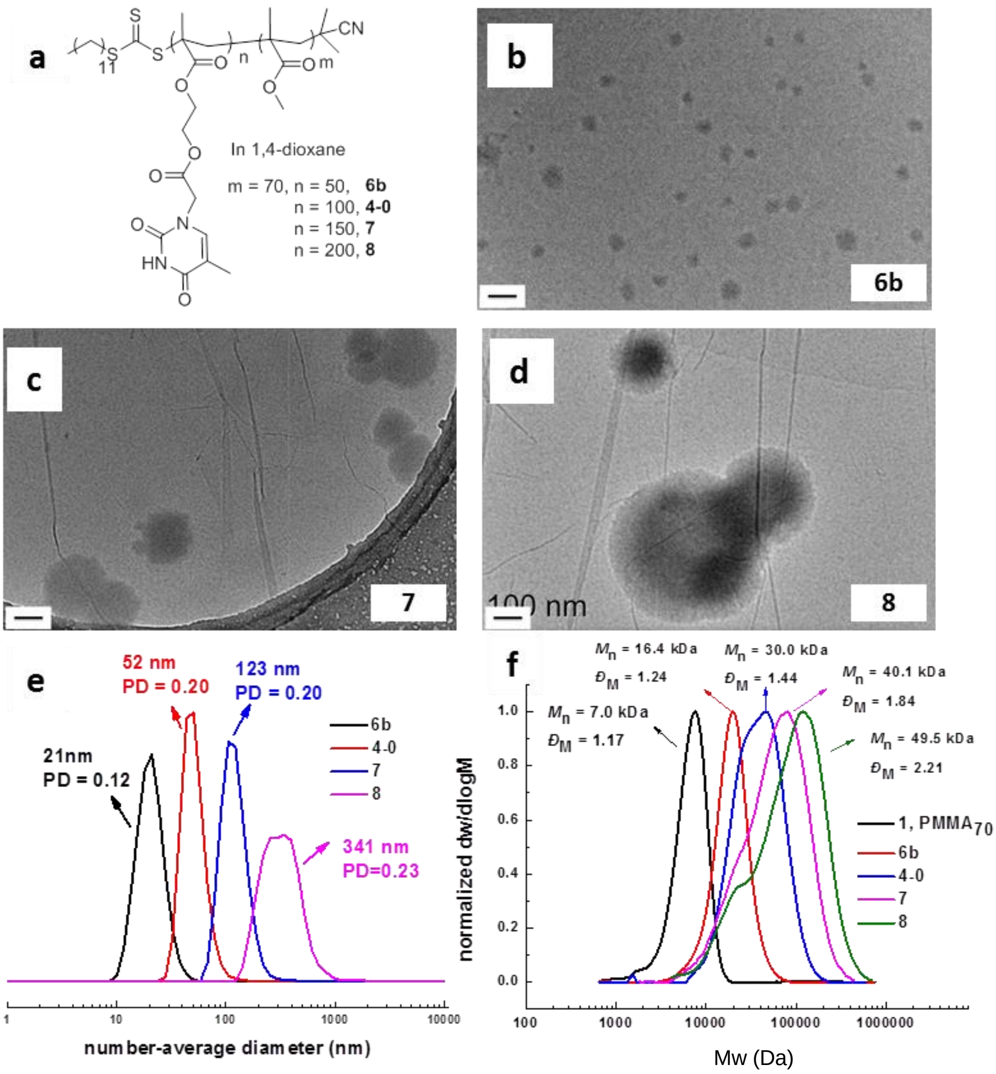


Figure S19. Characterization of the self-assemblies prepared by RAFT dispersion polymerization in 1,4-dioxane for a target copolymer $PMMA_{70}$-*b*-$PTMA_n$, their corresponding structures (a), representative TEM images (b - d), DLS particle size distributions (e) and SEC traces (f) with increasing TMA block length (DMF as eluent, PMMA standards). Scale bar: 100 nm.

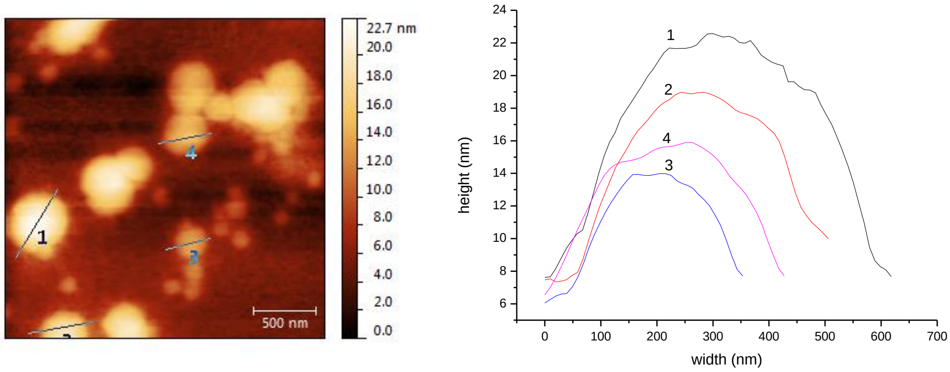


Figure S20. AFM height image of the self-assembly prepared in the polymerization **7**, $PMMA_{70}$-*b*-$PTMA_{150}$ in 1,4-dioxane and the corresponding height profile.

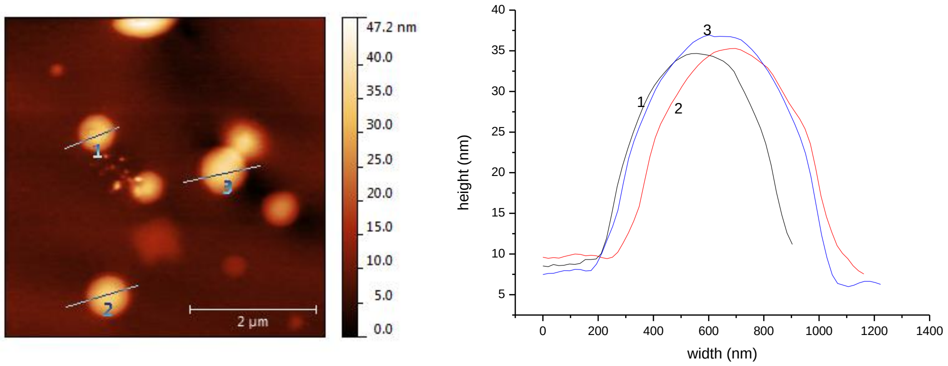


Figure S21. AFM height image of the self-assembly prepared in the polymerization **8**, $PMMA_{70}$-*b*-$PTMA_{200}$ in 1,4-dioxane and the corresponding height profile.

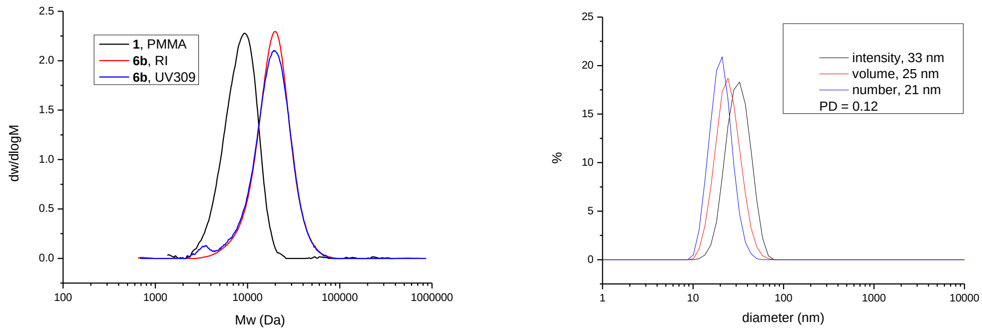


Figure S22. SEC analysis of **6b** (DMF eluent, with PMMA standards) and DLS analysis of the self-assembly prepared from **6b**, $PMMA_{70}$-*b*-$PTMA_{50}$ in 1,4-dioxane.

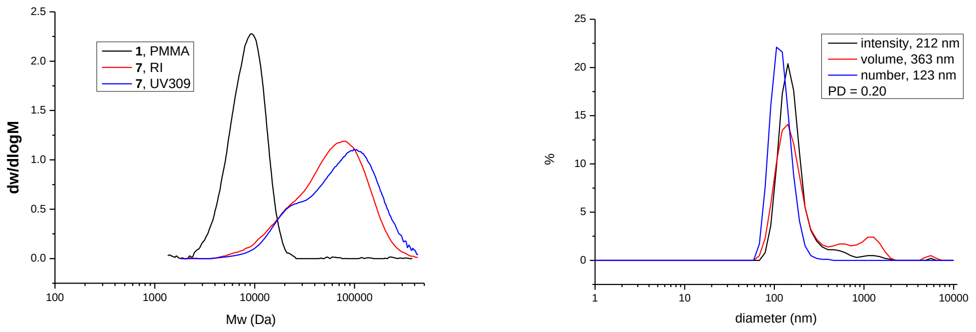


Figure S23. SEC analysis of **7** (DMF eluent, with PMMA standards) and DLS analysis of the self-assembly prepared from **7**, $PMMA_{70}$-*b*-$PTMA_{150}$ in 1,4-dioxane.

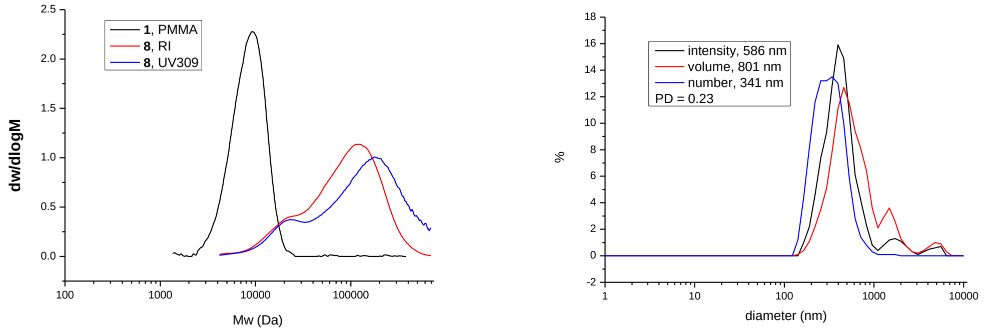
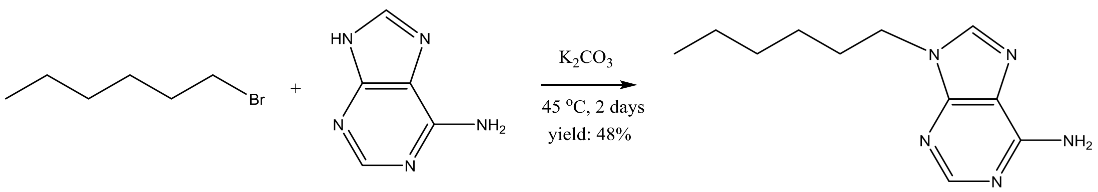
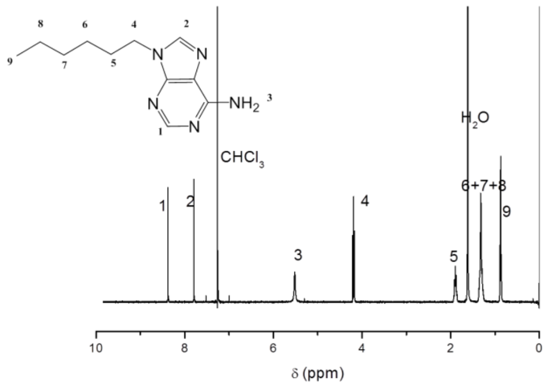


Figure S24. SEC analysis of **8** (DMF eluent, with PMMA standards) and DLS analysis of the self-assembly prepared from **8**, $PMMA_{70}$-*b*-$PTMA_{200}$ in 1,4-dioxane.

10. Analysis of the polymers formed in the presence of an adenine mediator



Scheme S1. Synthetic route for the preparation of the adenine-containing mediator.



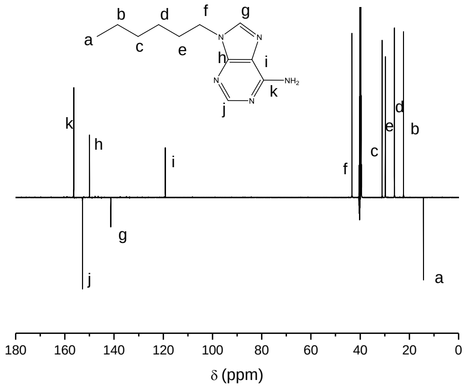
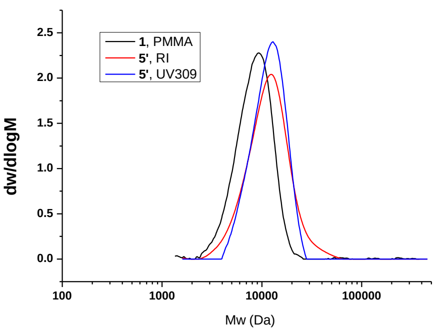


Figure S25. ^{1}H NMR (in $CDCl_3$) and ^{13}C NMR (in DMSO-d_6) spectra of adenine-containing mediator.



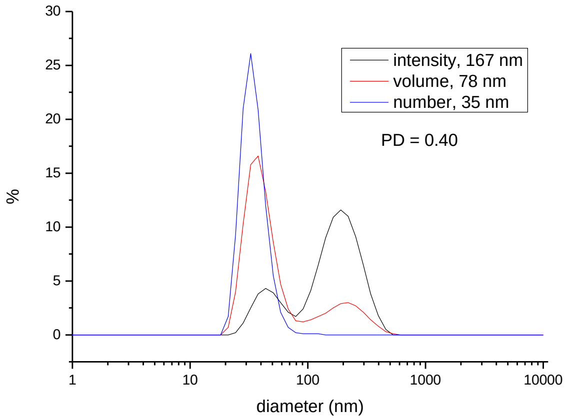


Figure S26. SEC traces of **5'** (DMF eluent, with PMMA standards) and DLS analysis of the self-assembly prepared from **5'**, $PMMA_{70}$-*b*-$PTMA_{20}$ in the presence of adenine mediator in chloroform.

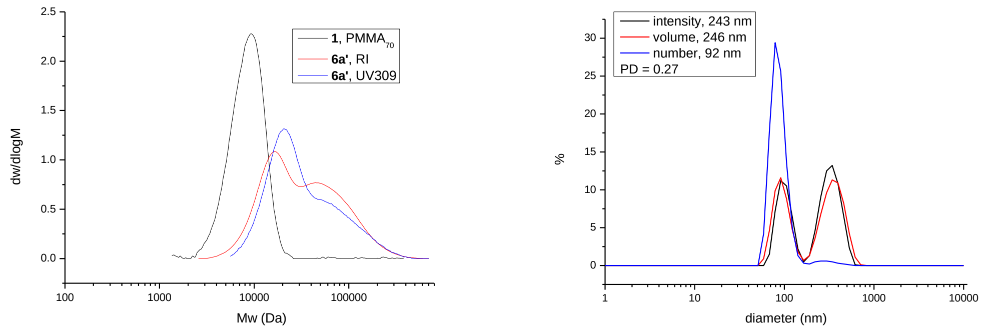


Figure S27. SEC traces of **6a'** (DMF eluent, with PMMA standards) and DLS analysis of the self-assembly prepared from **6a'**, $PMMA_{70}$-*b*-$PTMA_{50}$ in the presence of adenine mediator in chloroform.

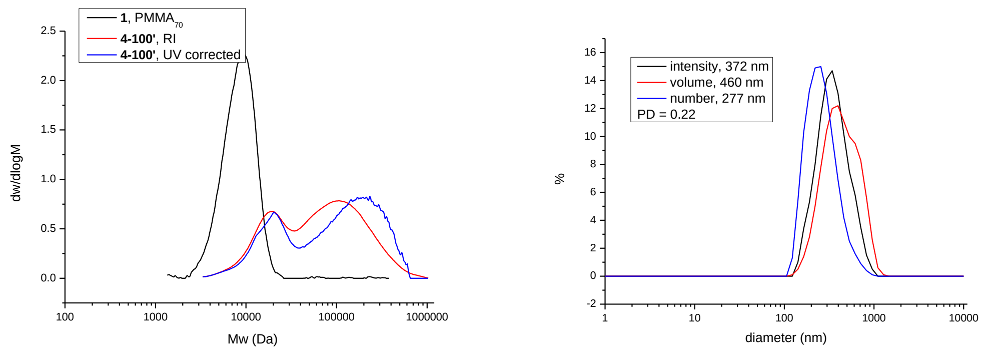


Figure S28. SEC analysis of **4-100'** (DMF eluent, with PMMA standards) and DLS analysis of the self-assembly prepared from **4-100'**, $PMMA_{70}$-*b*-$PTMA_{100}$ in the presence of adenine mediator in chloroform.

11. Analysis of the polymers formed from macro-CTA, 3

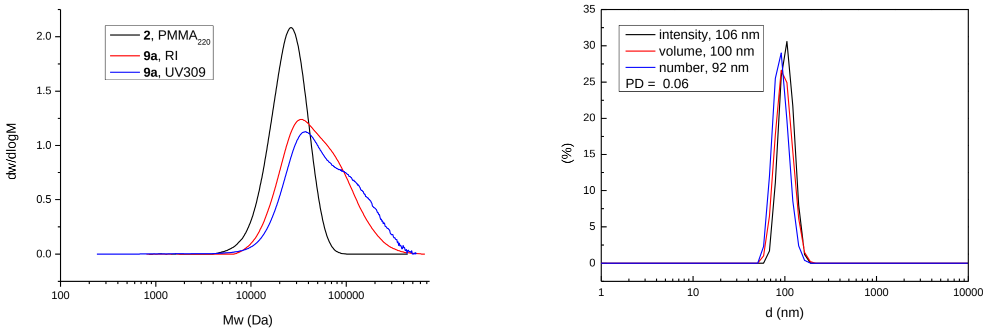


Figure S29. SEC analysis of **9a** (DMF eluent, with PMMA standards) and DLS analysis of the self-assembly prepared from **9a**, $PMMA_{220}$-*b*-$PTMA_{50}$ in chloroform.

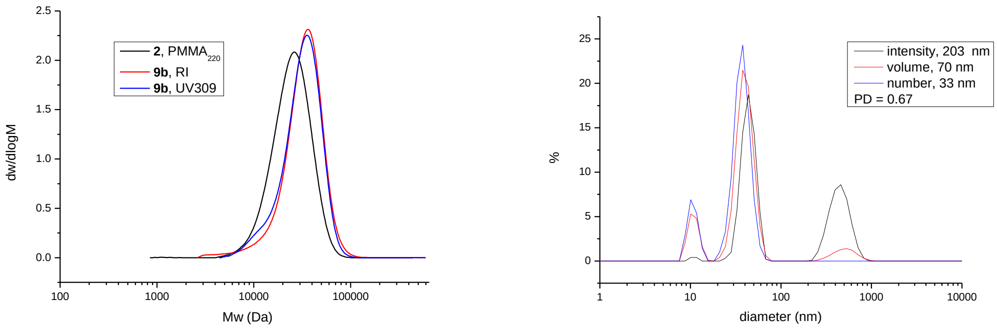


Figure S30. SEC analysis of **9b** (DMF eluent, with PMMA standards) and DLS analysis of the self-assembly prepared from **9b**, $PMMA_{220}$-*b*-$PTMA_{50}$ in 1,4-dioxane.