Electronic Supplementary Information

PDMAEMA-b-PLMA-b-POEGMA triblock terpolymers via RAFT polymerization and their self-assembly in aqueous solutions

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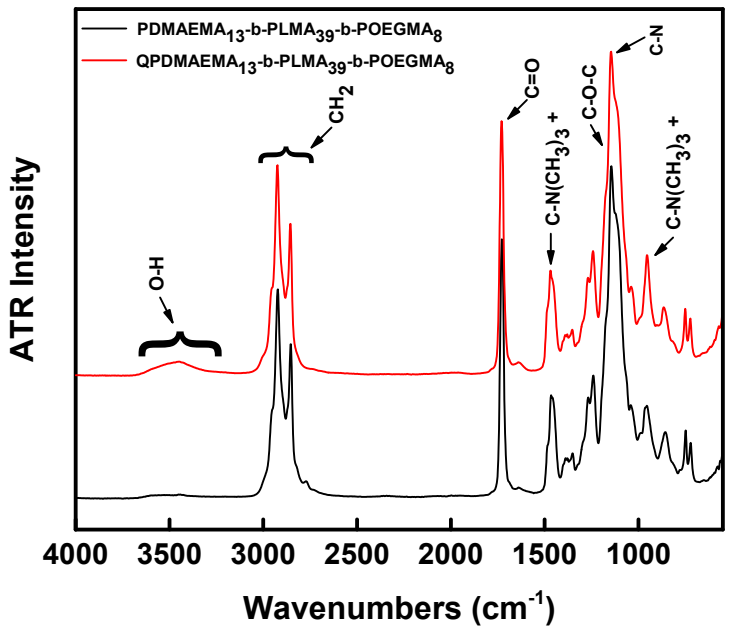

Figure S1. Comparative ATR-FTIR spectra for samples $PDMAEMA_{13}$-b-$PLMA_{39}$-b-$POEGMA_8$ (black) and $QPDMAEMA_{13}$-b-$PLMA_{39}$-b-$POEGMA_8$ (red).

Table S1. DLS, SLS and FS results for $PDMAEMA_{13}$-b-$PLMA_{39}$-b-$POEGMA_8$ micelles in aqueous solutions using the solvent-switch (THF) and thin film solubilization protocols

Sample	Solubilization Protocol	$M_{w\ app}$[a] g/moL (x 10^6)	N_{agg}	R_h[b] (nm)	PDI[b]	CMC[c] g/mL (x 10^{-6})
$PDMAEMA_{13}$-b-$PLMA_{39}$-b-$POEGMA_8$	THF	1.66	1064	30	0.247	1.00
	Thin Film	9.42	6038	60	0.261	5.00
$QPDMAEMA_{13}$-b-$PLMA_{39}$-b-$POEGMA_8$	THF	1.14	65	77	0.458	5.08
	Thin Film	1.31	7507	148	0.384	2.85

[a] Determined by SLS. [b] Determined by DLS at 90°. [c] Determined by FS using pyrene as the probe.

From the data presented in Table S1 it can be concluded that neither additional solubilization protocol leads to the formation of simple core-shell micelles for sample $PDMAEMA_{13}$-b-$PLMA_{39}$-b-$POEGMA_8$. Apparently, the high PLMA content leads to the formation of rather kinetically frozen structures also in these cases with possibly a compound micelle structure as in the case of the direct dissolution protocol. In the case of $QPDMAEMA_{13}$-b-$PLMA_{39}$-b-$POEGMA_8$ the use of THF as a common solvent facilitates the formation of smaller core-shell micelles, and the higher water solubility of QPDMAEMA block may also support this self-organization route. It is interesting to note that CMC values are influenced by the protocol used in all cases pointing to a difference in internal structure of the micelles, formation route, as well as their capability for encapsulation of low molecular weight hydrophobic compounds (like the pyrene probe). Limiting values for I_1/I_3 ratio are below 1.2 in all cases, denoting a very non-polar environment for pyrene at higher terpolymer concentrations (Fig. S2) within the PLMA cores.

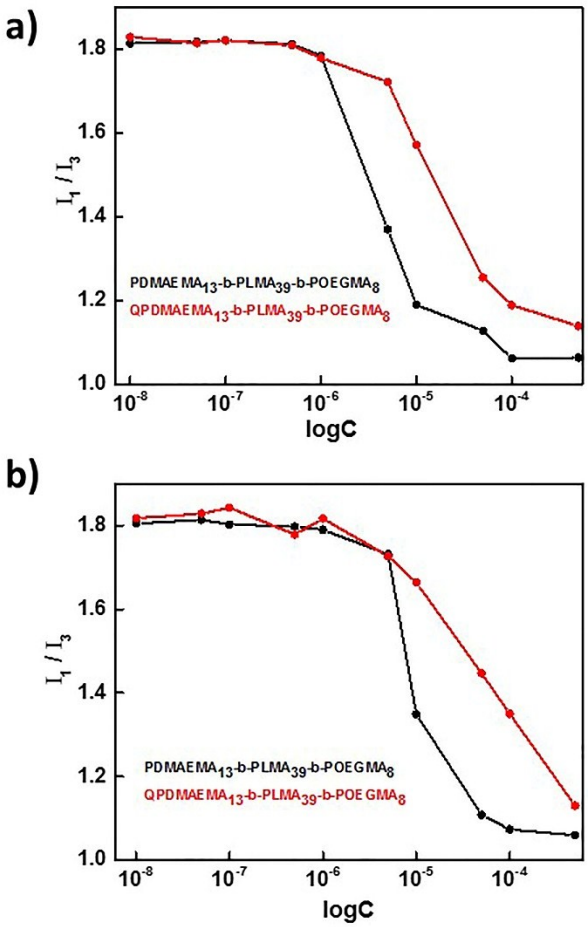

Figure S2. Comparative CMC determination graphs, from FS using pyrene probe, for samples $PDMAEMA_{13}$-b-$PLMA_{39}$-b-$POEGMA_8$ and $QPDMAEMA_{13}$-b-$PLMA_{39}$-b-$POEGMA_8$ for (a) solvent-switch (THF) and (b) thin film layer solubilization protocols.

Table S2. R_g/R_h ratio from SLD/DLS measurements for samples $PDMAEMA_{13}$-b-$PLMA_{39}$-b-$POEGMA_8$ and $QPDMAEMA_{13}$-b-$PLMA_{39}$-b-$POEGMA_8$ for all solubilization protocols

Sample	Solubilization protocol	R_g[a]	R_h[b]	R_g / R_h
$PDMAEMA_{13}$-b-$PLMA_{39}$-b-$POEGMA_8$	H_2O	125	72	1.73
	THF	84	30	2.8
	Thin Film	100	60	1.66
$QPDMAEMA_{13}$-b-$PLMA_{39}$-b-$POEGMA_8$	H_2O	75	71	1.05
	THF	70	78	0.9
	Thin Film	153	148	1.03

[a] Determined by SLS. [b] Determined by DLS.

Light scattering results on the R_g/R_h ratio (Table S2) indicate the presence of spherical micelles in the solutions of samples $PDMAEMA_{13}$-b-$PLMA_{39}$-b-$POEGMA_8$ and $QPDMAEMA_{13}$-b-$PLMA_{39}$-b-$POEGMA_8$, except maybe for the case of sample $PDMAEMA_{13}$-b-$PLMA_{39}$-b-$POEGMA_8$ assemblies from THF solutions, where R_g/R_h values point to the existence elongated structures may be formed, something that is not confirmed by SEM observations however. In the case of sample $QPDMAEMA_{13}$-b-$PLMA_{39}$-b-$POEGMA_8$ solutions the presence of vesicles cannot be excluded, although the N_{agg} values are low and do not conform to vesicular structures, which usually have a larger aggregation number.

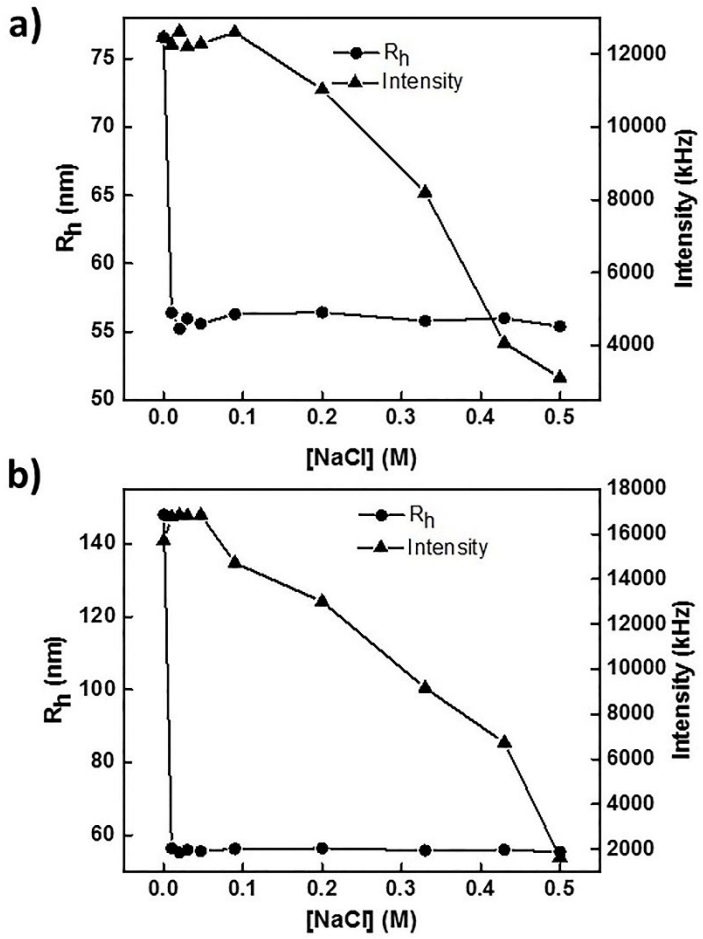

Figure S3. R_h and scattered intensity as a function of ionic strength ([NaCl]) for $QPDMAEMA_{13}$-b-$PLMA_{39}$-b-$POEGMA_8$ using (a) THF and (b) thin film layer solubilization protocols.

The ionic strength dependence of size and mass of sample $QPDMAEMA_{13}$-b-$PLMA_{39}$-b-$POEGMA_8$ self-organized structures seems to be independent of the solubilization protocol utilized. In any case a disintegration of the nanostructures is observed by increasing ionic strength of the aqueous solution, as in the case of the direct water solubilization protocol (see also discussion in the main manuscript).