PDEGMA-b-PDMAEMA-b-PLMA triblock terpolymers and their cationic analogues: Synthesis, stimuli responsive self-assembly and micelleplex formation

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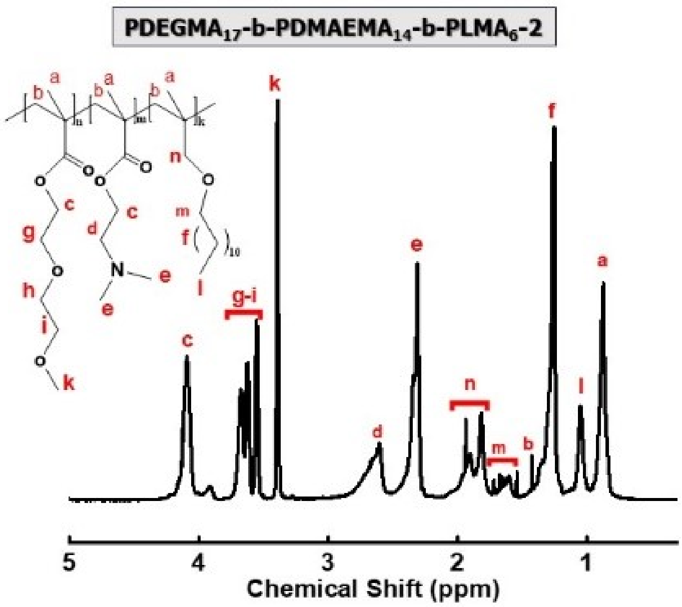

Figure S1: [1]H-NMR spectrum for PDEGMA$_{17}$-b-PDMAEMA$_{14}$-b-PLMA$_{6}$-2 triblock terpolymer in $CDCl_3$ solvent.

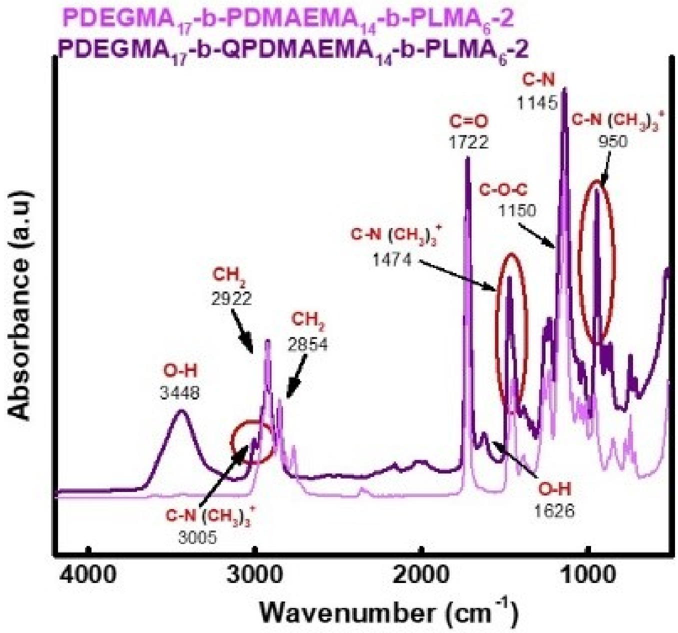

Figure S2: FT-IR spectra of PDEGMA$_{17}$-b-PDMAEMA$_{14}$-b-PLMA$_6$-2 terpolymer and the corresponding PDEGMA$_{17}$-b-QPDMAEMA$_{14}$-b-PLMA$_6$-2 quaternized terpolymer.

CMC determination

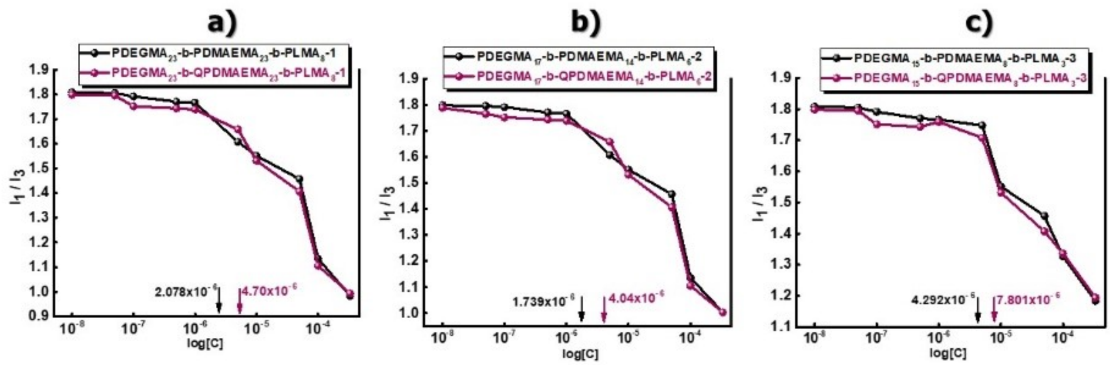

Figure S3: CMC determination for terpolymers PDEGMA$_{23}$-b-(Q)PDMAEMA$_{23}$-b-PLMA$_8$-1 (a), PDEGMA$_{17}$-b-(Q)PDMAEMA$_{14}$-b-PLMA$_6$-2 (b) and PDEGMA$_{15}$-b-(Q)PDMAEMA$_8$-b-PLMA$_3$-3 (c).

The determination of the critical micelle concentration (CMC) of the synthesized triblock terpolymers (amine-based and quaternized amine) was achieved via fluorescence spectroscopy using pyrene as the fluorescent probe. The terpolymer solutions with concentrations varying from 1.0×10^{-8} g/mL to 5.0×10^{-4} g/mL were prepared and the I_1/I_3 relative intensity ratio of pyrene probe was calculated. The representative graphs of the I_1/I_3 ratio versus the polymer concentration before and after the chemical modification reaction are depicted in Figure S3. The extracted CMC values for all terpolymer solutions are listed in Table 2. A plateau can be clearly noticed in the lower concentration region, where the micelles have not been formed yet and also the transition region can be observed at higher concentration values where the formation of micellar nanostructures is evident. It can be noticed that the quaternized polymers exhibit somehow higher CMC values. This may be explained by the fact that after chemical modification of the PDMAEMA block the quaternized terpolymers present enhanced solubility in water and hence micellar structures should be formed at higher concentrations.

The CMC values are lower for the terpolymers that contain a higher amount of the PLMA hydrophobic block, which is anticipated since the higher the hydrophobic content the lower the concentration required for the formation of micellar nanostructures. For instance, for terpolymers $PDEGMA_{23}$-b-(Q)$PDMAEMA_{23}$-b-$PLMA_8$-1 (Figure S3 a) and $PDEGMA_{17}$-b-(Q)$PDMAEMA_{14}$-b-$PLMA_6$-2 (Figure S3 b), the CMC values are lower because of the high hydrophobic PLMA block content. In the higher concentration regions, the I_1/I_3 ratio values are less than 1.2, indicating a fairly hydrophobic environment for the pyrene molecules in the core of the formed micelles, which is composed of the hydrophobic PLMA blocks.[1,2]

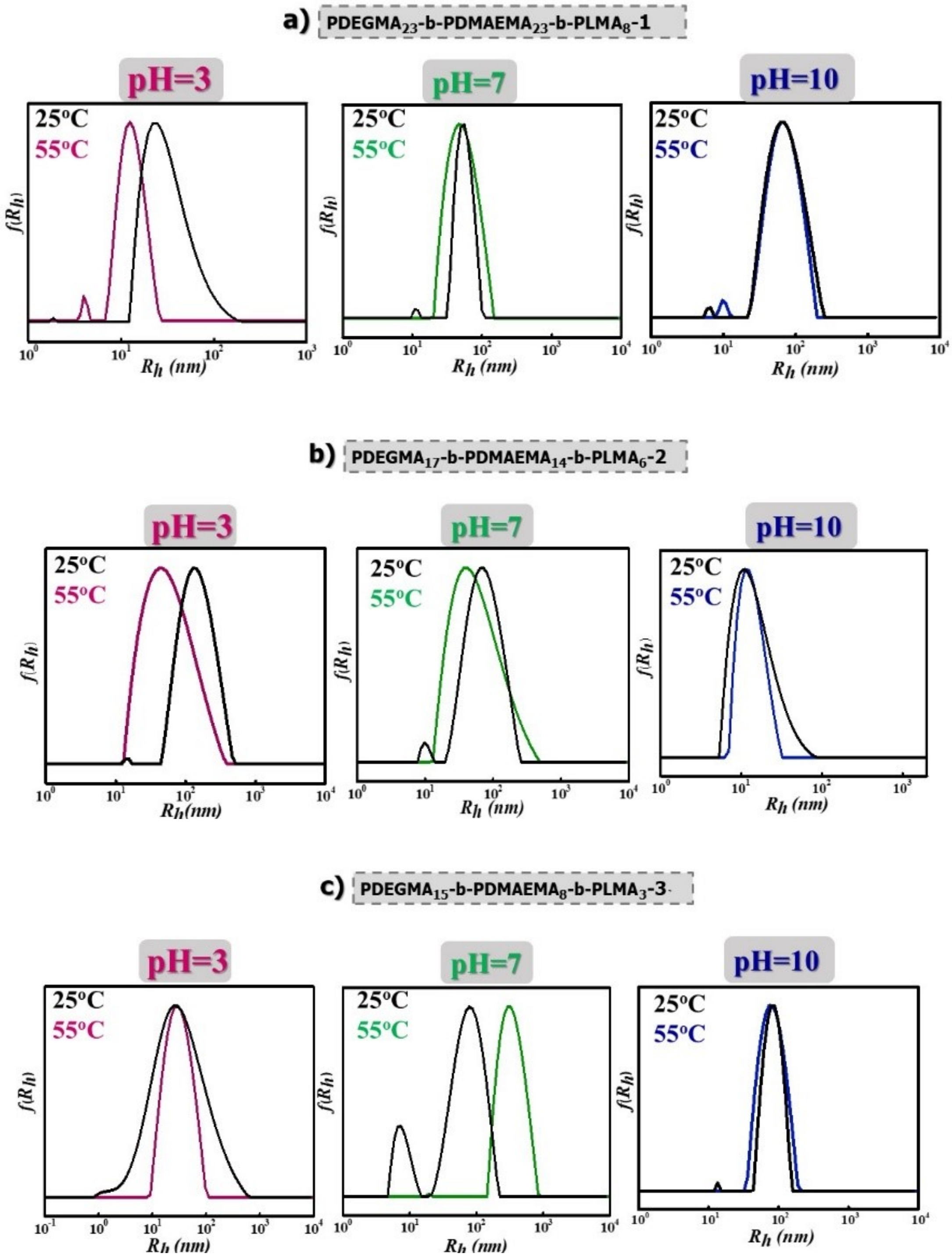

Figure S4: Size distributions from Contin analysis for triblock terpolymers in aqueous solutions at pH=3, 7, 10 and at selected temperatures (measuring angle 90°).

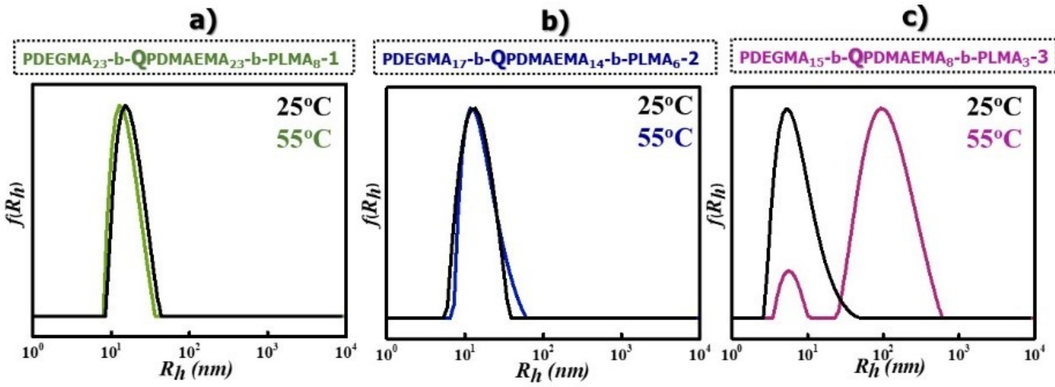

Figure S5: Size distributions from Contin analysis for $PDEGMA_{23}$-b-$QPDMAEMA_{23}$-b-$PLMA_8$-1 (a), $PDEGMA_{17}$-b-$QPDMAEMA_{14}$-b-$PLMA_6$-2 (b) and $PDEGMA_{15}$-b-$QPDMAEMA_8$-b-$PLMA_3$-3 (c) quaternized triblock terpolymers at selected temperatures.

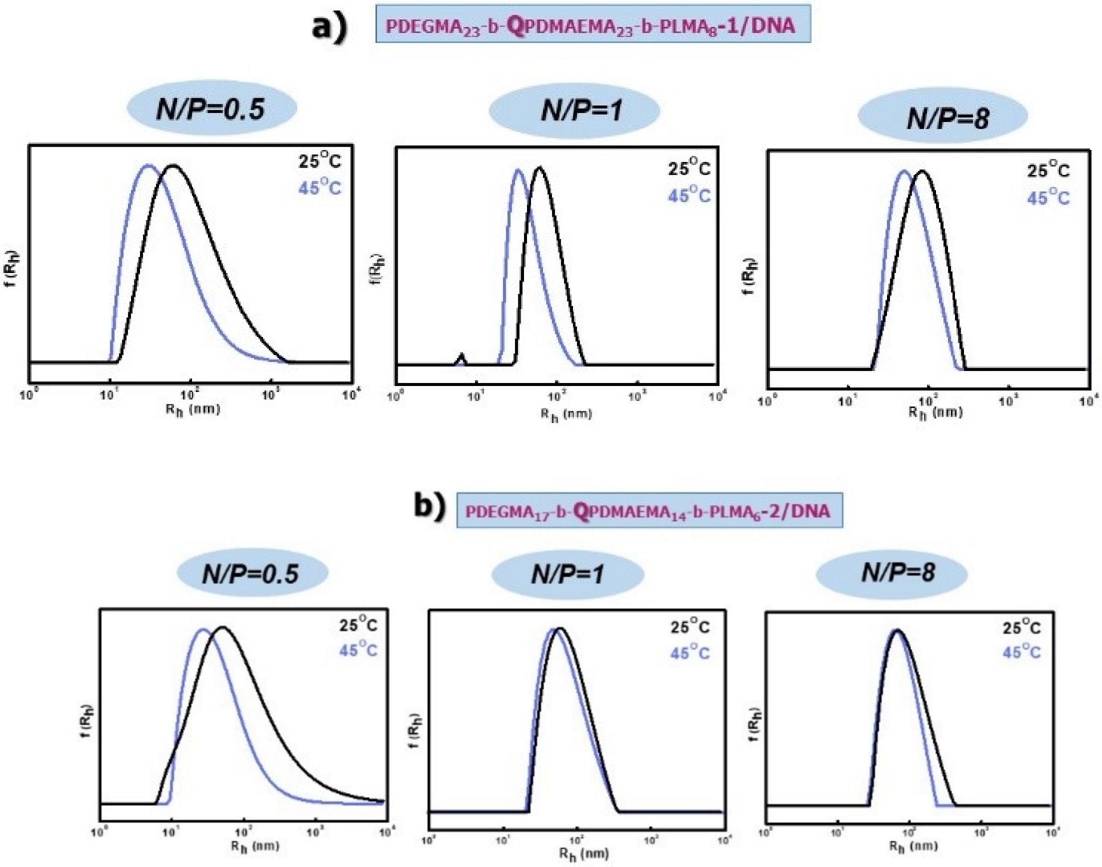

Figure S6: Size distributions from Contin analysis for PDEGMA$_{23}$-b-QPDMAEMA$_{23}$-b-PLMA$_8$-1/DNA (a) and PDEGMA$_{17}$-b-QPDMAEMA$_{14}$-b-PLMA$_6$-2/DNA (b) at various N/P ratios and at selected temperatures.

References

1. J.-F. Gohy, Block Copolymer Micelles, *Advances in Polymer Science*, 2005, **190**, 65-136.

2. F.M. Winnik, H. Ringsdorf, J. Venzmer, Langmuir, 1991, **7**, 905-91.