Supporting information

pH-responsive PDMS-b-PDMAEMA micelles for intracellular anticancer drug delivery

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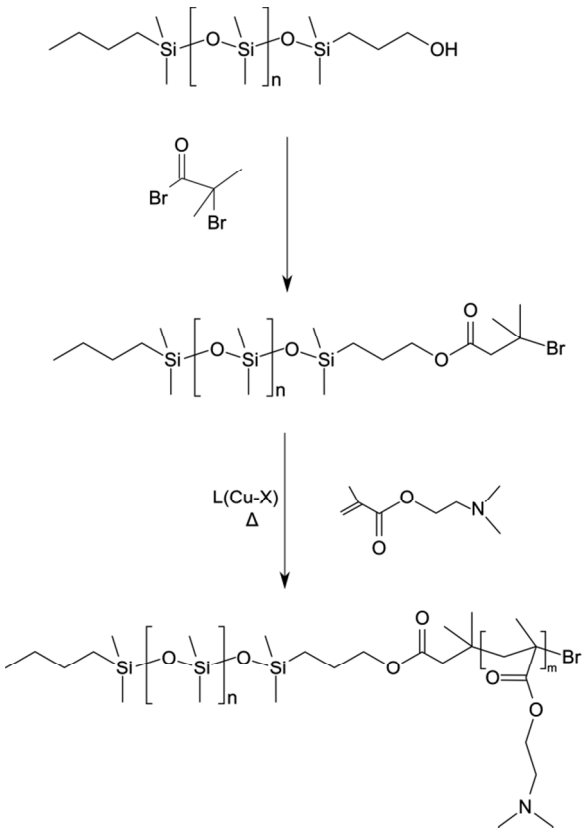
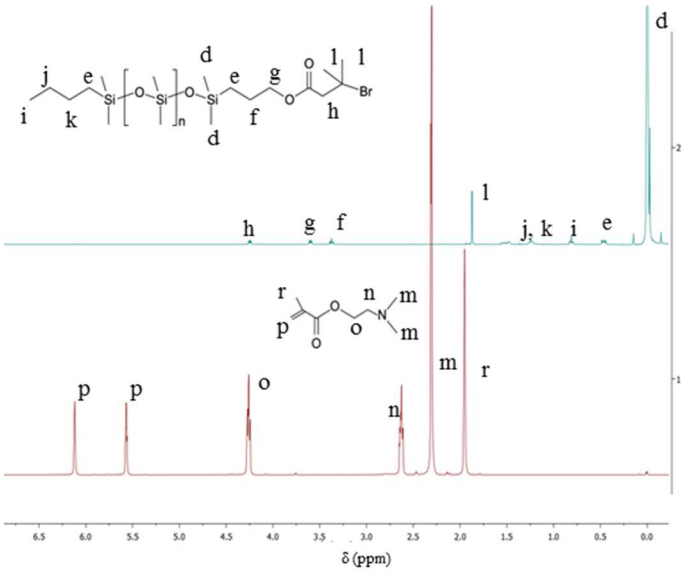
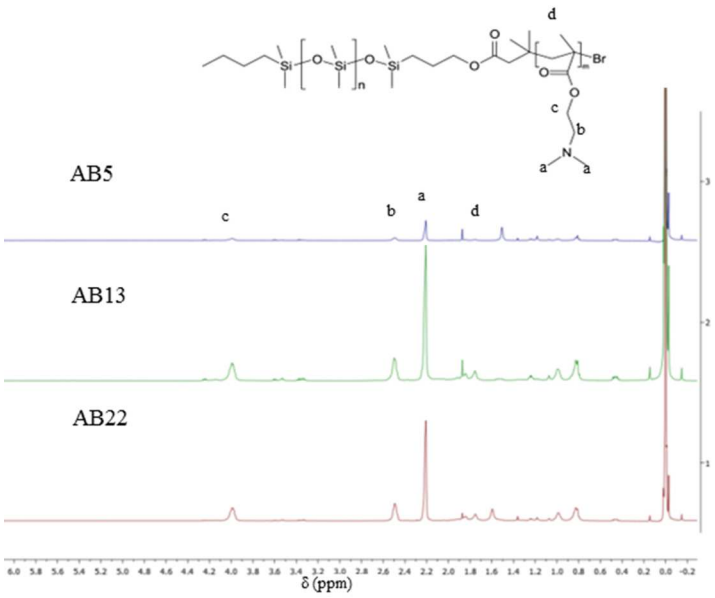


Figure/Scheme S1: Synthesis of PDMS-*b*-PDMAEMA block copolymers



A)



B)

Figure S2: ^{1}H NMR spectrum of A) PDMS macroinitiator and DMAEMA, B) PDMS-*b*-PDMAEMA block copolymers.

In ^{1}H NMR spectrums can be seen increased signals of methyl protons present in tertiary amine groups of PDMAEMA at δ 2.2 and additional two times alkyl protons of the chain (at δ 2.5 and δ 4). Hydrogen protons presented in DMAEMA at δ 5.6 and δ 6.2 are despaired as a clear evidence of monomer conversion.

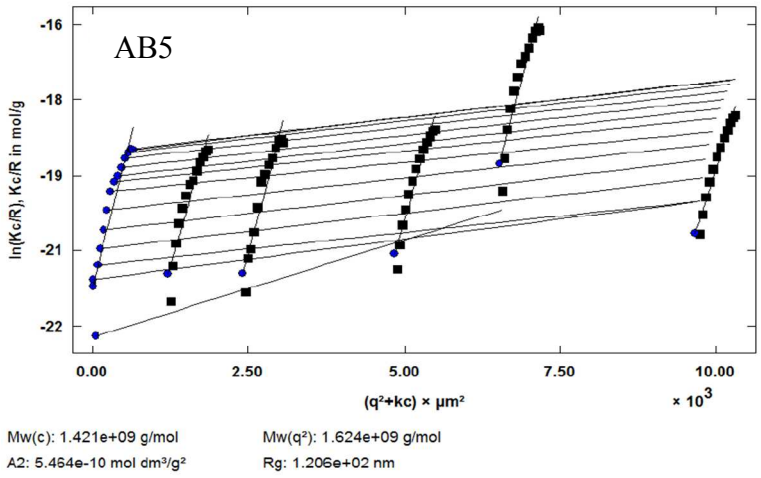


Figure S3: Guinier plot of static light scattering data of AB5 nanocarriers.

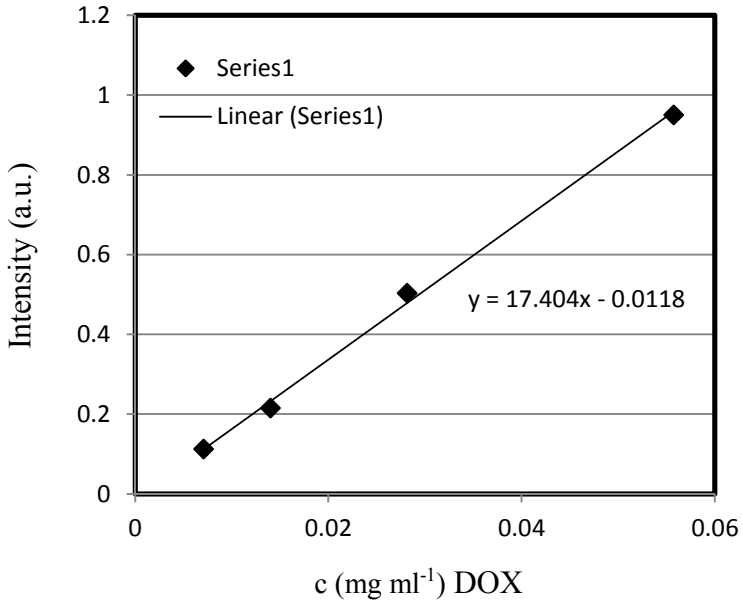


Figure S4: Determination of extinction coefficient of DOX.

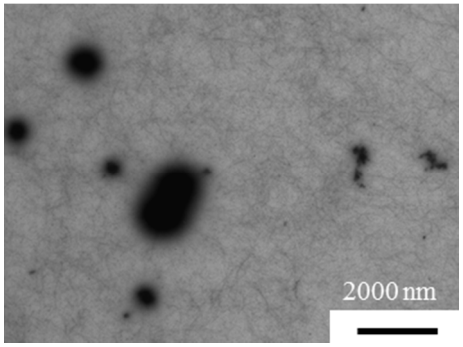


Figure S5: TEM image of DOX after 3 days of incubation.

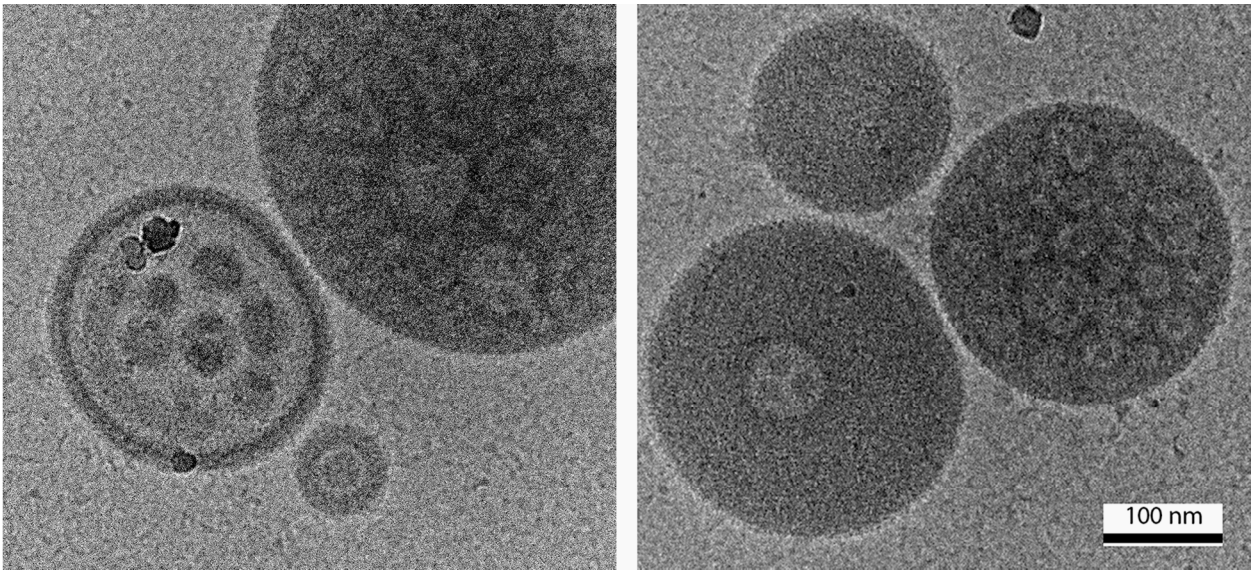


Figure S6: Cryo-TEM image of AB5 particles at pH 5.5 (left) and pH 7.4 (right) showing presences of vesicular and multi-compartment particles. (same scale apply to both images)

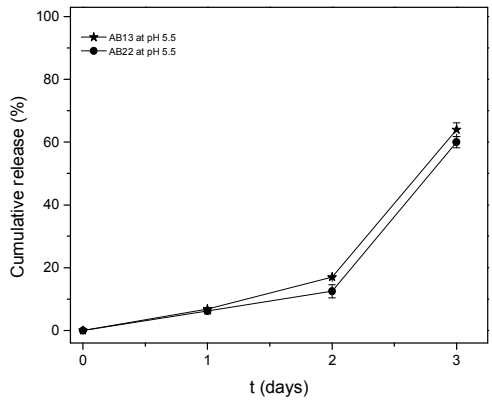


Figure S7: Cumulative release of AB13-DOX and AB22-DOX loaded micelles.

In the case of AB13 and AB22 particles slower DOX release was observed. The charge is giving stability to the particles. Longer are chains, higher is density of the charge, therefore also the IEP (iso electric point) is shifting toward higher value. The chains of PDMAEMA are getting protonated upon lowering pH and density of positive charge is increasing. Consequently the

repulsion between the chains in the same particles and also repulsion between the different particles is enhanced, leading to overall higher stability of colloidal solution. In the case where is PDMAEMA (5 units) short, is the protonation (repulsion between the PDMAEMA chains) on hydrophobic core much more pronounced than in the case of longer chains. Indeed that longer chains have higher density of charge but also higher flexibility since the chains are longer and consequently causing less tension to the core. In addition, also the influence of the counter ions present in the buffer play important role. They “sit” between the charged chains and present hindrance of the charge that is also becoming more pronounced with increased length of the PDMAEMA. Thus is the release of DOX slower in the case of longer PDMAEMA chains (more stabilized structure in PBS) and not faster as would seem to first sign.

In addition, for the encapsulation efficiency calculation, the value of DOX concentration after two days of intensive dialysis at pH 7.4 was used. In the case of AB13 particles was calculated encapsulation efficiency of DOX approx. 20% and for AB22 particles 16 %, respectively. The encapsulation efficiency of DOX is decreasing with increasing of PDMAEMA block. This is due to the fact that longer cationic PDMAEMA block hinder encapsulation of positive charged DOX.