Functional triblock terpolymers for vesicle self-assembly and decoration of polymer microgels towards membrane confinement

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By combining hydrogels or coacervates with amphiphiles, cell-like systems can be generated [1] . While the use of natural lipids offers the advantage of more closely mimicking biological membranes, the use of synthetic block co- and terpolymers provides greater flexibility in terms of membrane thickness, stability, and chemical modification. [2] On this account this work explores the synthesis of various triblock terpolymers, their self-assembly in aqueous solution, as well as their interaction with microgels to decorate their surface with a membrane for tailor-made transport.

Using various RAFT agents, triblock terpolymers are synthesized, consisting of a hydrophilic *N* -isopropylacrylamide (NIPAM) block, a hydrophobic hydroxypropyl acrylate (HPA) block, and cationic blocks of 4-vinylpyridine (pH-sensitive) or [2-(Methacryloyloxy)ethyl] trimethylammoniumchloride (TEMA). Both their molecular structure and PDI are investigated using ^{1}H, ^{13}C and 2D HSQC NMR as well as SEC, and their self-assembly is examined using DLS at various pH values. These studies indicate the formation of self-assembled structures in a size range of approx. 260 nm or 650 nm, depending on the terpolymer used. The exact type of structure is currently being investigated via small-angle X-ray scattering.

Furthermore, we use a 4VP $_{10}$ -HPA $_{70}$ -NIPAAM $_{40}$ terpolymer equipped with a thioxothiazolidine as a reactive end group, which allows for subsequently attaching various functional groups, e.g., fluorescein or adamantane. The first is used as a probe for further characterization of the terpolymer/μGel assemblies, while the latter is employed to investigate the guided assembly of terpolymers on the microgel's surface by guest-host interactions between them and a β-cyclodextrine functionalization on the gels surface. To this end, hydrogels produced using droplet microfluidics in a cell-like size range of 50 μm have been incubated with a library of triblock terpolymers in various compositions (hydrophobic block length fixed at about 50 % with a varying amount of ionic block length ranging from 9 – 19 %, at molar masses of about 12,000 – 18,000 g/mol depending on the terpolymer), and the resulting assemblies are examined using confocal microscopy. These studies indicate a strong influence of the different terpolymer structures on their self-assembly behaviour and furthermore hint towards significant interaction between the terpolymer assemblies and the μgels, which will be explored in detail in further studies.

Keywords:
Triblock terpolymers, Self-assembly, Host-Guest interactions, Microgels

References:

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