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pH-responsive Vesicles Based on A Hydrolytically Self-cross-linkable Copolymer

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1. Introduction

Amphiphilic block copolymers can form a range of supramacromolecular assemblies with spherical, cylindrical and vesicular morphologies.[1-2] Water-dispersible polymeric vesicles are more durable than conventional liposomes and hence are promising nano-sized vehicles for the protection and delivery of water-soluble drugs and proteins. Recently, Du and Chen reported a range of cross-linked vesicles based on poly(ethylene oxide)-*block*-poly[3-(trimethoxysilyl)propyl methacrylate] (PEO-*b*-PTMSPMA) copolymers in either methanol/water or DMF/water mixtures.[3-6] Lecommandoux et al. reported polypeptide-based block copolymer vesicles whose size[7] responded to changes in the solution pH. In related work, Deming and co-workers described a new type of stimulus-responsive polypeptide vesicle by conformation-specific assembly.[8] Herein we report a new type of shape-persistent polymeric vesicle with pH-tunable membrane permeability. These vesicles are formed by the self-assembly of a pH-responsive, hydrolytically self-crosslinkable copolymer, poly(ethylene oxide)-*block*-poly[2-(diethylamino)ethyl methacrylate-*stat*-3-(trimethoxysilyl)propyl methacrylate], [PEO-*b*-P(DEA-*stat*-TMSPMA)], in THF/water mixtures.

2. Materials and Methods

This block copolymer was synthesized by statistical copolymerization of 2-(diethylamino)ethyl methacrylate (DEA) and 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) in methanol at room temperature using a poly(ethylene oxide)-based macro-initiator and a standard Atom Transfer Radical Polymerization (ATRP) protocol.[9] This route gave much lower polydispersities (M_w/M_n = 1.10-1.20) than those reported for the statistical copolymerization of methyl methacrylate with TMSPMA in anisole at 70 °C using a similar PEO_{45} macro-initiator (M_w/M_n = 1.58-1.78).**Hiba! A könyvjelző nem létezik.** The resulting colloidally stable vesicles were characterized by ^{1}H NMR, transmission electron microscopy (TEM), dynamic laser light scattering (DLS) and stopped-flow fluorescence experiments.

3. Results and Discussion

TEM confirmed the successful preparation of polymer vesicles. DLS confirmed the vesicle diameter responded to the solution pH. The stopped flow technique indicated that the permeability of the vesicle walls was sensitive to the pH of the aqueous solution, as expected. Gold-decorated vesicles were obtained by *in situ* reduction of $AuCl_4^-$ anions to produce gold nanoparticles within the vesicle walls. Full results and discussion was published in J. Am. Chem. Soc. 2005.[10]

4. Conclusion

In summary, new block copolymer vesicles were prepared from self-assembly of a hydrolytically self-crosslinkable block copolymer in THF/water mixtures. DLS and fluoresence studies indicate that the permeability of the vesicle walls is pH-sensitive. These vesicles can also be decorated with gold nanoparticles; this provides further structural insights and may offer some possibilities for vesicle-supported precious metal catalysts and for good contrast agent for in vivo imaging if used as delivery carriers.

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