

Engineering thermo-responsive NanoSuitcases

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Introduction

The objective of this study is to develop thermo-responsive nano-constructs. The approach followed in the past to render nano-particles with the ability to respond to small temperature differentials, aimed at grafting thermo-responsive chains onto the surface of various nanoparticles [1] or blending them with a non-responsive matrix [2]. Expectedly, these nano-particles displayed a very limited ability to respond to temperature changes since a non-responsive component was part of the system.

This contribution introduces totally thermo-responsive hollow nano-structures, comprising only poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblocks [3]. The uniqueness of these novel nano-sized constructs stems from their ability to display a remarkable and reversible change in size (up to 1000 times by volume), within a narrow temperature interval. These supramolecular architectures are produced by cross-linking intramolecularly end-capped PEO-PPO-PEO dimethacrylates, while these amphiphilic triblocks are constrained to the specific spatial configuration dictated by their micellar organization.

Materials and Methods

(I) *Pluronic F-127 dimethacrylate* [4]. The PEO-PPO-PEO dimethacrylate derivatives (F127-DMA) were obtained by the reaction of the native OH-terminated PEO-PPO-PEO triblock with methacryloyl chloride. The functionalization of the triblock was demonstrated by ¹H-NMR analysis and FTIR spectroscopy. Once F127-DMA formed micelles in aqueous medium, they were crosslinked intramolecularly by free radical polymerization, using ammonium persulfate, ferrous sulfate and L-ascorbic acid.

(II) *Biodegradable NanoShells* were obtained, by the ring opening polymerization of L-lactide, initiated by the terminal hydroxyl groups of F-127, followed by the incorporation of the methacrylate moieties.

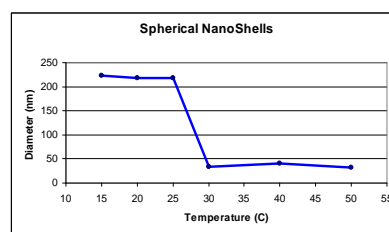
(III) *Dynamic Light Scattering*. The average hydrodynamic radius of the microstructures present in the aqueous medium was measured by dynamic light scattering (HPPS, HPP5001, Malvern Instruments, U.K).

(IV) *Transmission electron microscopy*. Samples were lyophilized with liquid nitrogen and then re-dissolved in water prior to use and dried on the grid.

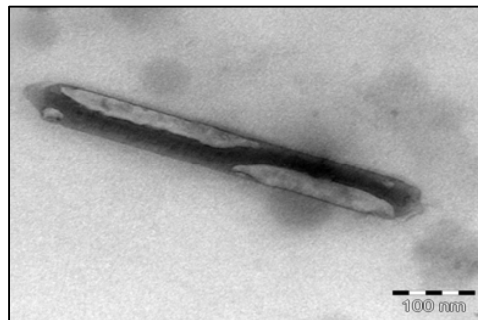
Results and Discussion

The cross-linking of the hydrophilic PEO shell, not only stabilized the micelles, resulting in extremely robust nano-constructs but rendered them also with a unique dimensional reverse thermo-responsive behavior. F127 triblocks appear as molecular unimers at low temperatures and they form a micelle, at a higher temperature. For example, at 15 °C, the size of F127 unimers is 6-7 nanometers, while its micelles attain a size of around 20 nanometers, at 40 °C. Once the temperature decreases

below *cmt*, the micelles disassemble, reverting to their unimeric state. In fundamental contrast to the above, the affixed nano-sized constructs engineered decrease in size markedly when going from a lower temperature to a higher one, in a sharp and essentially reversible manner. Spherical Nano-Shells formed at 50 °C exhibited a diameter of around 200 nanometers at 15°C, while displaying a markedly smaller size (approximately 30 nanometers in diameter) at 40°C, as shown in the figure below.



Since the shape and size of the micelles depend on the temperature, Nano-Shells having various geometries, were "sculptured" by performing the cross-linking reaction at different temperatures. Tubular nano-shells were formed by crosslinking rod-like micelles at 80°C. Their size shifted from 3000 nanometer at 15°C, to around 300 nanometers at 40°C (as shown in the figure below).



Work was also devoted to impart to these NanoShells additional features, such as pH-responsiveness, and biodegradability.

References

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