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Phosphate-Functionalized Stabilized F127 Nanoparticles: Introduction of Discrete Surface Charges and Electrophoretic Determination of Aggregation Number

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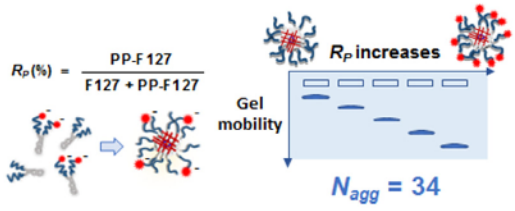
Abstract: Pluronic F127 forms spherical micelle with a defined number of molecules aggregated in aqueous environments. Such self-assembled micelles dissociate into unimers below certain concentration and temperature. We stabilized the micelles by semi-interpenetrating network (sIPN) formation within the hydrophobic core in the presence of a fluorescent dye. Additionally, by varying the mixing ratio of negatively charged and pristine F127s we prepared thermally stable polymeric nanoparticles with discrete surface charges within nearly same sizes. Using the nanomaterials with prescribed number of charges, we demonstrate that the electrophoretic mobility of nanoparticles is solely depending on number of surface charges. Finally, the aggregation number (N_{agg}) of F127 was further determined by electrophoresis.



Keywords: self-assembly, encapsulation, polymer aggregates, Pluronic, sIPNs.

1. Introduction

Pluronic block copolymers, so-called poloxamers, have been used as nonionic surfactants in diverse industries for several decades. The names given to the Pluronic family depend on the appearance of the substance (*i.e.*, flake, paste, and liquid) and the hydrophilic-lipophilic balance (HLB) (see Figure S1).[1] Of over 20 Pluronic products, F127 has gained considerable interest due to its high HLB value, which favors its use as an additive for water-friendly applications such as personal healthcare, detergents, and biomedicine.[2-4]

Particular amphiphilic block copolymers such as Pluronic, poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (PEO-*b*-PPO-*b*-PEO), spontaneously form nanosized micelles in aqueous media above their critical micelle temperature (CMT) and/or critical micelle concentration (CMC).[5,6] While the micelle core can interact with hydrophobic payloads, the two termini of all Pluronics with hydroxyl groups can be synthetically modified to various functional groups such as halides, thiol, amine, and acid, making the polymers ideal candidates for customized applications.[7,8] Above the CMT and CMC, the defined number of polymers form the spherical micelle; this number represents the aggregation number (N_{agg}). In polymer aggregate systems, the number of functionalized end-groups within a confined volume can greatly influence the physical properties of materials. For this reason, several methods have been developed to determine N_{agg}, such as fluorescence quenching, fluorescence correlation spectroscopy, and light scattering. However, a somewhat different method is required to determine the N_{agg} value of each specific Pluronic.[9-11] Interestingly, despite widespread use of F127 (PEO_{100}-*b*-PPO_{65}-*b*-PEO_{100}), various aggregation numbers have been determined, ranging from 10 to 80 and depending on the conditions and methods used to determine the N_{agg} of the polymer.[12-15]

In this study, thanks to discretely charged nanoparticles herein, we developed a new electrophoretic method to determine the N_{agg} of F127 using materials with prescribed net charges. First, micelles consisting of pristine F127 and phosphorylated F127, where the hydroxyl end-groups of F127 were converted into phosphate (Figure 1(A)), were blended at different volume ratios to

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