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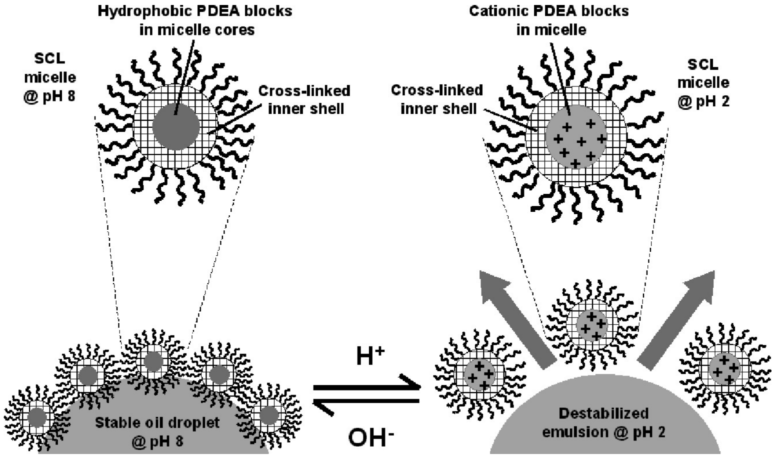

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# Syntheses of Shell Cross-Linked Micelles Using Acidic ABC Triblock Copolymers and Their Application as pH-Responsive Particulate Emulsifiers

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Colloidal particles have been used to prepare and stabilize emulsions (so-called “Pickering” or “Ramsden” emulsions) for over a century.[1] Most of this literature is concerned with various types of *inorganic* particles, such as silica, barium sulfate, or calcium carbonate, although recently there have been several interesting examples of *organic* latexes being used as emulsifiers.[2] In principle, particulate emulsifiers offer more reproducible formulations, reduced foaming problems, and lower toxicity profiles compared to conventional surfactants. Given that the formulation of emulsions is important for various industrial sectors, it seems likely that particulate emulsifiers will become more widely used in the future.

Since the pioneering work by Wooley and co-workers,[3] shell cross-linked (SCL) micelles have been examined by several research groups.[4,5] These fascinating organic nanoparticles offer the ability to design surface functionality for various applications. Of particular relevance to this work, we have shown that the use of stimulus-responsive ABC triblock copolymers allows the convenient preparation of SCL micelles with tunably hydrophilic micelle cores at relatively high solids.[5]

Herein, we describe the synthesis of novel SCL micelles from new acidic ABC triblock copolymers (see Figure 1) and their evaluation as pH-responsive particulate emulsifiers for a polar oil, 1-undecanol (see Figure 2). According to Binks, the energy required to displace a particulate emulsifier from the oil−water interface decreases rapidly with particle size.[1c] Given the relatively small size of SCL micelles (typically 10−50 nm diameter), it is interesting to ask whether such organic nanoparticles allow the formation of stable emulsions. Moreover, since SCL micelles can be designed to have pH-responsive cores, we wished to examine whether efficient demulsification could be achieved by simply varying the solution pH.

The poly[(ethylene oxide)-*block*-glycerol monomethacrylate-*block*-2-(diethylamino)ethyl methacrylate] (PEO-PGMA-PDEA) triblock copolymer precursor was synthesized by sequential monomer addition using atom transfer radical polymerization (ATRP) as described by Liu et al. (see Supporting Information).[5c] Esterification of the hydroxyl groups on the PGMA blocks using a 2-fold excess of succinic anhydride (SA) produced carboxylic acid-based SAGMA residues, and workup yielded the final zwitterionic PEO-PSAGMA-PDEA triblock copolymer precursor.[5f] Dissolution of these triblock copolymers at pH 9 led to the formation of near-monodisperse PDEA-core micelles of 21 nm diameter, with anionic PSAGMA inner coronas and PEO outer coronas. The carboxylic acid groups on the PSAGMA blocks were cross-linked using 1 molar equiv of 2,2′-(ethylenedioxy)bis(ethylamine), followed by the addition of 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide methiodide activator (2-fold excess based on the SAGMA groups[3c,d]). The outer shell of PEO chains prevents intermicellar fusion via a steric stabilization mechanism,[5d] hence ensuring exclusively intramicellar cross-linking even at the relatively high copolymer concentration of 5.0 w/v % used in this work. Dynamic light scattering studies indicated SCL micelle intensity average diameters of 30 nm at pH 9 and 36 nm at pH 2.5. The larger diameter at low pH is due to swelling caused by protonation of the core-forming PDEA blocks.

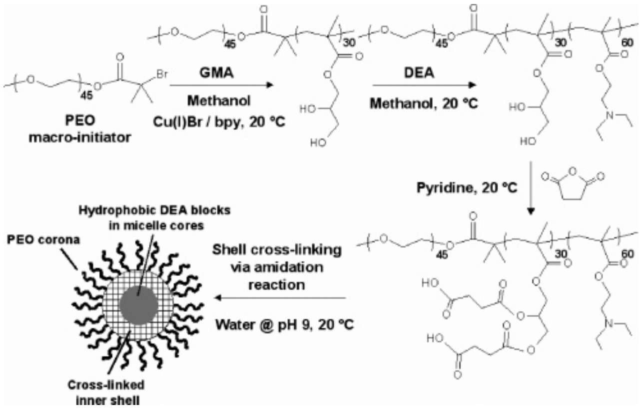

***Figure 1.*** Preparation of pH-responsive shell cross-linked micelles using a PEO-PSAGMA-PDEA triblock copolymer prepared by ATRP. Shell cross-linking was conducted by amidation chemistry.[3c]

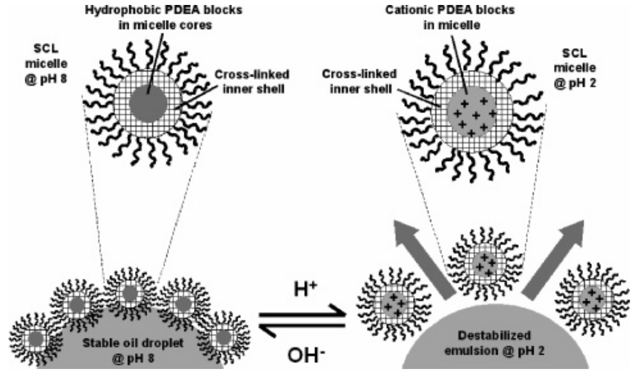

***Figure 2.*** Schematic representation of pH-induced emulsification and demulsification using shell cross-linked micelles as particulate emulsifiers. Dewetting from the oil droplet surface occurs at low pH.

Stock solutions (1.0 wt % solids) of the SCL micelles were prepared by serial dilution of the SCL micelle solution after extensive dialysis. The solution pH of 5.0 mL aliquots of these SCL micelle solutions was adjusted to either pH 2−3 or pH 8−9 using either HCl or NaOH. These solutions were then homogenized with 5.0 mL of 1-undecanol for 2 min at 20 °C using an IKA Ultra-Turrax T-18 homogenizer with a 10 mm dispersing tool operating at 12 000 rpm. Emulsion stabilities after standing for 24 h at 20 °C were assessed by visual inspection. Stable emulsions were obtained using the SCL micelles as a “Pickering”-type emulsifier at pH 8−9 (see Figure 3 and Supporting Information). Conductivity measurements indicated that 1-undecanol-in-water (i.e. o/w) emulsions were obtained, and this emulsion type was confirmed using the drop test. Optical microscopy studies revealed spherical, polydisperse oil

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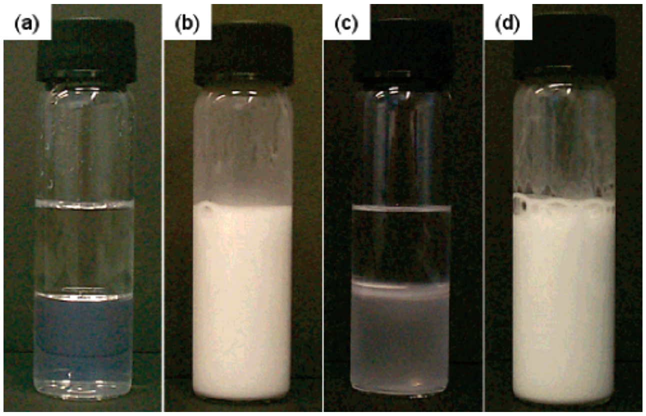

***Figure 3.*** Digital photographs illustrating the reversible emulsification and demulsification of a 50:50 mixture of 1-undecanol and water using PEO-PSAGMA-PDEA-based shell cross-linked micelles: (a) before homogenization, (b) after homogenization at pH 9, (c) rapid macroscopic demulsification caused by the addition of one drop of 1 M aqueous HCl solution to the emulsion shown in (b), (d) after rehomogenization at pH 9.

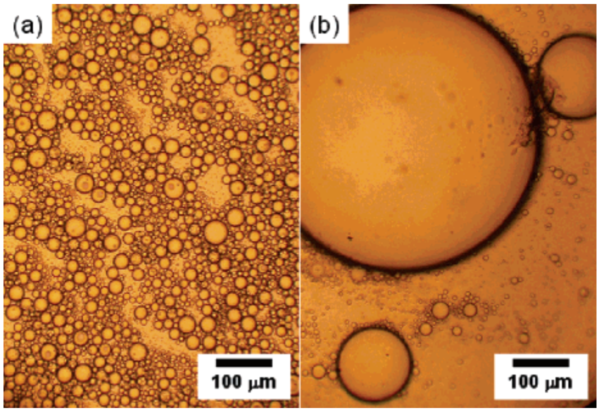

***Figure 4.*** Optical micrographs of 1-undecanol emulsion droplets prepared at pH 9 and 20 °C using PEO-PSAGMA-PDEA shell cross-linked micelles (target degree of cross-linking = 100%): (a) before and (b) 30 s after the addition of one drop of 1 M aqueous HCl solution to the emulsion. The large increase in droplet size indicates rapid droplet coalescence, which precedes macroscopic phase separation.

droplets (see Figure 4a). The mean oil droplet diameter measured using a Malvern Mastersizer 2000 instrument was 18 $\mu$m. Thus, these emulsions are generally somewhat finer than those previously obtained under the same conditions using a 160 nm diameter sterically stabilized polystyrene latex as a particulate emulsifier.[2c−e] Perhaps more importantly, only water-in-1-undecanol (or w/o) type emulsions were obtained using the polystyrene latex emulsifier under essentially the same conditions. Presumably this is related to the differing wettability of the SCL micelles compared to that of the sterically stabilized latex particles.[1c]

The 1-undecanol-in-water emulsion prepared using SCL micelles was demulsified (coalesced) by lowering the solution pH of the aqueous phase to pH 2−3 with aqueous HCl, followed by gentle agitation at 20 °C (see Figure 3). This is presumably because the SCL micelles acquire swollen cationic nanogel character as the hydrophobic PDEA chains in the micelle cores become hydrophilic on protonation (see Supporting Information). Hence, the SCL micelles no longer wet the droplet interface and become detached from it, leading to unstable droplets, rapid coalescence, and macroscopic phase separation. Optical microscopy studies recorded during the in situ addition of HCl confirmed that rapid droplet coalescence occurred (see Figure 4), and Malvern Mastersizer data indicated that the concentration of 18 $\mu$m 1-undecanol droplets in the measuring cell unit decreased rapidly after addition of HCl due to coalescence (see Supporting Information). This emulsification−demulsification cycle is reversible (see Figure 3) and essentially the same droplet diameter was obtained on rehomogenization (see Supporting Information).

In contrast, control experiments using the *uncross-linked* PEO-PSAGMA-PDEA triblock copolymer confirmed that relatively large 1-undecanol-in-water emulsions were obtained at both pH 2−3 (70 $\mu$m diameter) and pH 8−9 (45 $\mu$m diameter). Presumably, this is because the PDEA blocks are hydrophobic at high pH, whereas at low pH the nonionized PSAGMA blocks become hydrophobic. Thus the uncross-linked triblock copolymer is adsorbed at the oil−water interface at both high and low pH (as either a soluble emulsifier or a particulate (micellar) emulsifier). Moreover, our attempts to break the emulsion formed by the uncross-linked triblock copolymer at pH 8 by addition of acid only led to partial (60%) demulsification. Hence cross-linking clearly enhances the performance of this new class of particulate emulsifier.

In summary, we describe the first use of SCL micelles as pH-responsive particulate emulsifiers. Control experiments clearly demonstrate that shell cross-linking enhances the performance of these new organic nanoparticles since the uncross-linked ABC triblock copolymer micelles are much less effective pH-responsive emulsifiers. These SCL micelles produce relatively fine o/w emulsions compared to the w/o emulsions produced by latex-based emulsifiers or o/w emulsions produced by the uncross-linked triblock copolymer under the same conditions.

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**Supporting Information Available:** Synthesis and characterization details for the SCL micelles. Summary table of emulsion properties. Droplet size data for 1-undecanol-in-water emulsions. This material is available free of charge via the Internet at http://pubs.acs.org.

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