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# Emulsions stabilized with organic solid particles

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ABSTRACT

Biodegradable and biocompatible o/w emulsions were prepared using triglyceride oil and solid organic particles made of block copolymer nanoparticles as stabilizers (Pickering emulsions). In order to reach high concentration of internal phase, rather concentrated dispersions of nanoparticles were required. Nanoparticles of poly(caprolactone)-*block*-poly(ethylene oxide) (PCL-*b*-PEO) diblock copolymer were obtained using the "nanoprecipitation" process relying of the spontaneous emulsification upon solvent shifting. The classical "nanoprecipitation" process was improved so as to afford more concentrated suspensions of nanoparticles, and the nanoparticles were characterized by means of dynamic light scattering and $^1$H NMR spectroscopy. The process allowed the preparation of aqueous dispersions of PCL-*b*-PEO nanoparticles with 35–50 nm diameter at concentrations over 5 wt.%. In $D_2O$, the PCL blocks formed a central hydrophobic core of reduced mobility, while the PEO blocks formed a hydrophilic corona layer swollen by water. O/w emulsions of medium chain triglycerides were successfully prepared using the suspensions of PCL-*b*-PEO nanoparticles as stabilizers. Typical droplet sizes were between 2 μm and 15 μm. The emulsions showed great stability upon storage and their particle size distributions did not show excess nanoparticles present in the aqueous phase as submicron nanoparticles, even when large amounts of nanoparticles with respect to oil were used. The mean droplet diameter of emulsions was controlled by the mass ratio *M*(oil)/*M*(nanoparticles). SANS and TEM experiments performed on PCL-*b*-PEO nanoparticles and micelle-stabilized emulsions disclosed a rearrangement of the nanoparticles at the oil/water interface due to the liquid state of the micelle core of PCL.


## 1. Introduction

Pickering emulsions are stabilized by solid particles in place of surfactants [1]. Their "surfactant-free" character makes them attractive for cosmetic and pharmaceutical application where surfactants often show adverse effects (irritancy, hemolytic behavior, etc.) [2]. Towards such domains, biocompatible and biodegradable Pickering emulsions would be an obvious benefit. They can be made up from the oils used in pharmaceutical applications, and organic solid particles made from biodegradable materials. Since solid stabilizing particles are necessarily smaller than emulsion droplets, solid particles of nanometric size were selected so as to allow the fabrication of Pickering emulsions over a wide droplet size range. There are two issues to be overcome in order to reach such goal: (i) the choice of organic nanoparticles that are partially wet by water and oil in order to ensure their anchoring to the oil/water interface; and (ii) the preparation of suspensions of solid particles of high enough concentration in order to allow full coverage of the droplet surface, even for concentrated emulsions of small droplets that have a large interfacial area. The purpose of the present research is the preparation of such emulsions stabilized by block copolymer nanoparticles. This can be achieved if the two issues quoted above receive satisfactory answer.

Solid particles can spontaneously adsorb at fluid interfaces forming either a dense monolayer of particles, or a thick layer of aggregated solid particles that behaves as a rigid stabilizing layer acting against coalescence [3,4]. Many types of solid particles (hydrophilic silica, hydrophobic silica, clay, barium sulfate, calcium carbonate, polystyrene, spores, etc.) [1,5–12] were used to stabilize emulsions.

Biodegradable nanoparticles would decrease the risk of toxicity already observed with a lot of common chemical surfactants and inorganic nanoparticles, and they are expected to create a barrier to diffusion that allows a controlled release of drug substances incorporated either in the oily layer or inside the polymeric nanoparticles. Poly(caprolactone)-*block*-poly(ethylene oxide) (PCL-*b*-PEO) copolymers have raised much interest because they are biocompatible and partly biodegradable [13–16]. The PCL block is made of biodegradable polyester, and the PEO block is a water-soluble polymer of low molar mass that is bioresorbable.

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