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Nano- and microparticles of gelled oil combining aminoacid-based low molecular weight organogelators and nonionic amphiphilic polysaccharides

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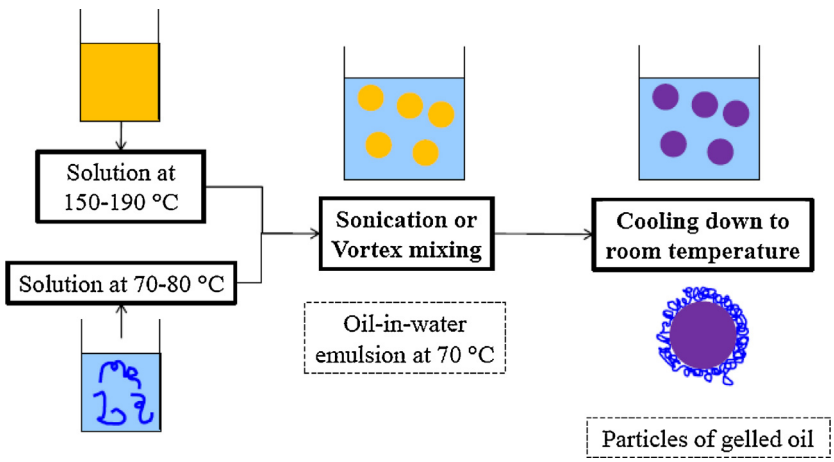
HIGHLIGHTS

- Aqueous suspensions of polysaccharide-covered particles of gelled oils were prepared.
- The mechanical behavior of gelled core was controlled using aminoacid-based gelator.
- Dissolution of organogelator in hot oil was followed by oil-in-water emulsification.
- By adjusting process conditions well-defined nano- and microparticles were obtained.
- The nature of gelled core was varied using one hydrocarbon oil and two triglycerides.

GRAPHICAL ABSTRACT



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ABSTRACT

Nano- and microparticles of gelled oils were prepared using an aminoacid-based low molecular weight organogelator and amphiphilic nonionic polysaccharides as stabilizers. The investigated oils were Tetralin, M810N and M829. The preparation procedure involved organogelator dissolution in hot solvent (150–190 °C) followed by oil-in-water emulsification at 70–80 °C in liquid state and final cooling step to room temperature to obtain gelled oil particles. The range of particle diameters (sub-micrometric or micrometric) could be adjusted by selecting the emulsification process, sonication or vortex mixing. Using sonication, organogel particles could be also prepared at room temperature with the oil phase in the gel form. The suspensions of gelled oil particles could be centrifuged and fully redispersed by vortex mixing with an increase of particle diameters whose extent depended on the nature of the oil.

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1. Introduction

Low-molecular weight organogelators (LMWO) were defined as small organic molecules (molar mass lower than 3000 g/mol)

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with the ability to self-organize in certain organic solvents, giving rise to the formation of fibrous networks that dramatically modify the flow properties of the medium [1]. Self-organization of gelator molecules occurred through the establishment of low energy interactions (for instance hydrogen bonds, ionic interactions, π-staking, dipole-dipole, solvophobic effects or van der Waals interactions). Among the properties of organogels, two common characteristics were of particular importance. First, the critical gelation concentration (CGC), i.e. the concentration above which gelation was observed at a given temperature. According to the chemical structure of the organogelator, CGC could be reduced down to values well below 0.5 wt%. This was a very interesting point for formulation applications. Second, organogels exhibited thermo-reversibility so that they recovered a liquid-like behavior when temperature exceeded a critical value (which depended on the concentration of organogelator). This property could be used to facilitate the flow of the mixture through pipes or to trigger drug release via viscosity variation for instance. Several studies have been reported about the formation and the mechanical properties of bulk organogels as well as about the links between molecular structure and macroscopic properties [2–7]. Nevertheless, there were much less reports about the use of organogelators in the formulation of disperse systems. Schematically, two types of colloidal dispersions have been reported involving organogels, according to the nature of the gelled phase. On the one hand, water-in-oil emulsions have been prepared in which the oil phase was gelled [8–15]. Gelling continuous oil phase prevented water droplets motion as well as coalescence and thus improved the colloidal stability of the dispersions. On the other hand, the preparation of aqueous suspensions of gelled oil particles has also been reported [16–25]. In that case, gelling disperse phase was closely related to specific applications. Researchers explored different ways of controlling the morphology of oil particles on the basis of the properties of the gelator. For instance by inducing an accumulation of the gelator at oil/water interface, capsules were obtained [16]. In another work, the gelator itself was designed so as to serve as chiral template [22]. In most of these formulations, the gelator was 12-hydroxystearic acid (HSA) with minimal concentrations of 0.5 wt% in the oil.

The design of new LMWO appeared as a promising track in formulation. Indeed innovation in the chemical structure of gelators would be a great opportunity to obtain dispersions with targeted end-use properties like polarity of gelled oil particles, size distribution, colloidal stability in various conditions, temperature reversibility... Some guidelines already existed to relate oil nature and required chemical characteristics of potential gelator candidates using Hansen and Hildebrand solubility parameters [26–32]. Nevertheless there were only a few studies in which colloidal properties of gelled oil dispersions were studied and all of them used HSA as the gelator [17,20].

Some of us reported the design and synthesis of a family of strong LMWO based on aminoacid derivatives [33,34]. Gelation of organic solvents was attributed to the formation of an entangled fibrillar network through hydrogen bonds and π-π stacking interactions [35,36]. A detailed analysis of oscillatory rheological properties of these organogels revealed that the macroscopic gel formation resulted from a jamming-induced gelation [37]. When cooling down the organic solution from the liquid state, organogelator molecules formed clusters below a certain temperature. These clusters started crowding when temperature further decreased. When temperature became lower than a critical value called gelation temperature ($T_{ORGANOGEL}$), the mechanical behavior of the system changed from liquid to solid-like. Below $T_{ORGANOGEL}$ the rheological behavior of the solution was that of a soft solid, with elastic modulus (*G*') higher than the loss modulus (*G*").

We already reported the preparation of nanometric and micrometric oil-in-water emulsions stabilized by amphiphilic polymers derived from polysaccharides (particularly from dextran, a non-ionic bacterial polysaccharide) [38,39]. The presence of a dense and thick superficial layer of hydrophilic loops at the surface of oil droplets provided good colloidal stability and offered the possibility of further chemical functionalization thanks to the reactive hydroxyl groups present at the surface. In addition, polysaccharide-covered oil droplets were used as templates for the preparation of polyester nanoparticles via emulsion-solvent evaporation procedure [40].

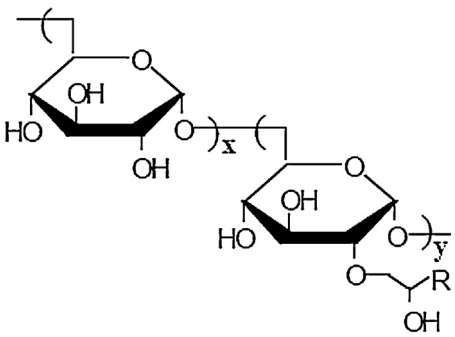

Fig. 1. Chemical structure of amphiphilic dextran derivatives, $DexC_6$-τ and $DexC_{10}$-τ. The degree of substitution was defined by $\tau = 100 \times y/(x + y)$. The linear aliphatic hydrocarbon group R was $—C_6H_{13}$ and $—C_{10}H_{21}$ for C_6 and C_{10} series, respectively.

In that work, we investigated the use of aminoacid-derived gelator molecules for the formulation of gelled oil particle suspensions stabilized by amphiphilic polymers derived from dextran. We particularly focused on the links between the formulation or process variables and the particle size distribution as well as colloidal stability of the suspensions. For the preparation of the particles, we selected three oils comprising two triglycerides currently used in pharmaceutical formulations. The targeted application of the particles was encapsulation of hydrophobic active substances. The presence of dextran chains at the surface of particles was intended for providing colloidal stability as well as opportunity to attach functional groups.

2. Experimental

2.1. Materials

All chemicals were purchased from Sigma-Aldrich® and used as received. The native dextran, T40® sample, had a weight-average molar mass close to 40,000 g/mol according to the provider. MilliQ® water was employed for preparing aqueous solutions. The hydrophobically modified dextrans used in that work were synthesized following a previously reported procedure [41]. Briefly, dextran T40® (10 g) was dissolved in 100 mL DMSO at room temperature. After 1 h, the required amounts of tetrabutyl ammonium hydroxide (TBAOH) and 1–2 epoxyoctane or 1–2 epoxydodecane were added to the solution. The reaction medium was stirred over 48 h at room temperature. The crude mixture was dialyzed against a 1:1 (v:v) mixture of deionized water and ethanol, followed by deionized water. The modified dextran was recovered by freeze drying and analyzed by ^1H NMR in DMSO d_6 in which a few drops of D_2O were added. The degree of substitution τ (%) was defined as the molar ratio (expressed in percents) of attached hydrocarbon groups to the number of glucose repeat units ($\tau = 100 \times y/(x + y)$ see Fig. 1). Polymers were named $DexC_6$-τ and $DexC_{10}$-τ where C_6 and C_{10} referred to the nature of hydrocarbon group. Hydrocarbon groups were assumed to be statistically distributed along polysaccharide backbone.

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