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Journal of Magnetism and Magnetic Materials 293 (2005) 1–7
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Superparamagnetic nanoparticles stabilized by polymerized PEGylated coatings

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Available online 2 March 2005

Abstract

Novel superparamagnetic iron oxide nanoparticles coated with polymerized PEGylated bilayers were prepared. Bilayers composed of 10-undecenoic acid (UD) inner and UDPEG (PEG ester of UD) outer layers are resistant to aggregation after γ-irradiation. Various methods of coating were developed to prepare small (60–100 nm) and ultrasmall (20–35 nm) particles without size separation processes.

Keywords: Superparamagnetism; Nanoparticles; Iron oxide; Bilayer; Poly(ethylene glycol); 10-Undecenoic acid; Synthesis; PEGylation

1. Introduction

Iron oxide nanoparticles offer valuable benefits in the in vivo biomedical applications due to their size-dependent superparamagnetism and non-toxic, metabolizable nature [1,2]. Superparamagnetic iron oxide nanoparticles are clinically used as contrast media in magnetic resonance imaging, and extensively evaluated for many applications such as magnetic drug delivery, cell tracking, hyperthermia [1,3–6]. These particles consist of iron oxide magnetic cores coated with a protective layer providing stability and dispersability, and yet are often in agglomerated form in a wide size range (from nanometer to micrometer). Isolation of the size fraction for appropriate application requires excessive fractionation steps including successive centrifugation at various g-forces for different particle sizes, magnetic fractionation at high gradient field and column separation [7]. Therefore, elimination of aggregation is a major issue to control the particle size and simplify the process. Aggregation during the particle processing and/or use is another significant problem and a function of particle stability. Aggregation of cores can be reduced by in situ coating of the magnetic cores with surface binding molecules. However, stability

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0304-8853/$ - see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.jmmm.2005.01.035

of the coated particles depends on the strength of the bond between core and coating. Coating materials are mostly adsorbed on the surface of the magnetic core, and may desorb at low concentrations causing particles to aggregate. Aggregation is a significant problem in most applications of magnetic nanoparticles.

Pharmacokinetics of particles is largely determined by size and surface and major limitations for in vivo applications of magnetic nanoparticles are large particle size, quick blood clearance and non-specific uptake by macrophages. Small particles (<50 nm) and polyethylene glycol (PEG) surfaces have been shown to be effective in extending blood circulation time. Yet, there are no simple methods to prepare stable aqueous suspensions of PEG-coated superparamagnetic nanoparticles in small sizes that eliminate the need for excessive size separation processes.

Here, we demonstrate the preparation of novel superparamagnetic iron oxide nanoparticles that are coated with two layers of interdigited and polymerizable surfactants. The inner layer is composed of a micelle forming ionic surfactant that covers the surface of the superparamagnetic core as a monolayer with the hydrocarbon tail extending out. The outer layer is composed of a non-ionic surfactant which is physically adsorbed on the inner layer and composed of a polymerizable hydrocarbon and a hydrophilic polymer, in particular PEG. Although few bilayer-coated particles such as gold and iron oxide have been reported recently, these systems are based on ionic surfactant bilayers that provide stabilization through electrostatic repulsion of the charged surfaces and do not contain PEG [8–10]. Tournier et al. [11] describe interwined layers of glycerophospholipids and pluronics, however, with an overall

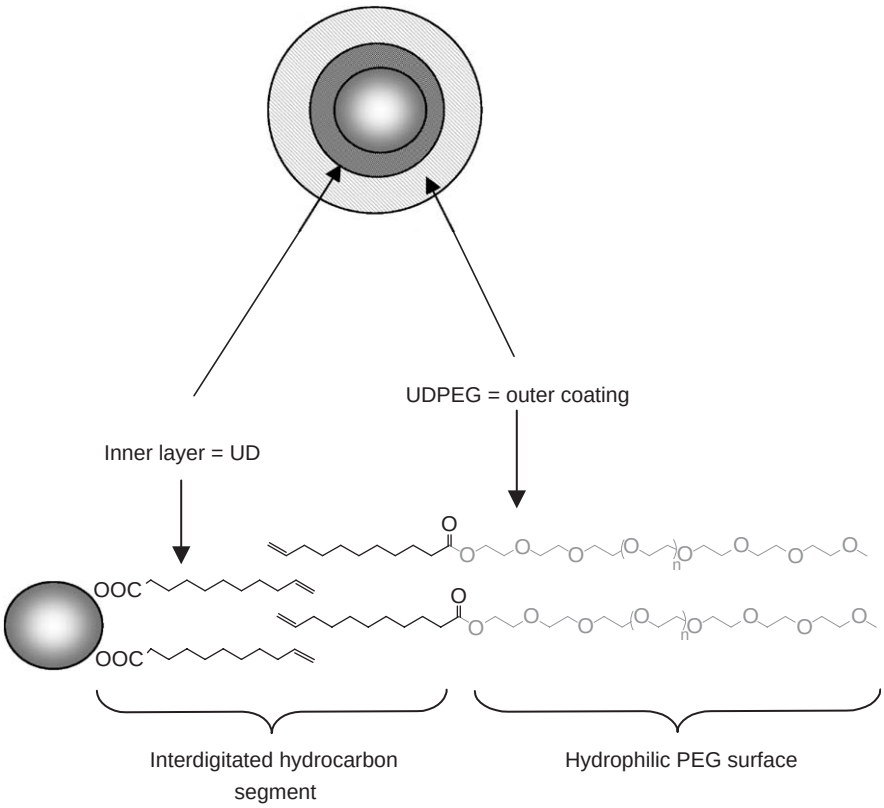

Fig. 1. Bilayer structure around magnetic core.