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Amphiphiles with polyethyleneoxide–polyethylenecarbonate chains for hydrophilic coating of iron oxide cores, loading by Gd(III) ions and tuning R_2/R_1 ratio

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ABSTRACT

The present work is aimed at the synthesis of hydrophilic colloids with convenient transverse and longitudinal NMR-relaxation times. Core-shell morphology with iron oxide cores and hydrophilic shell enriched by Gd(III) ions is the basis for the colloids with dual-mode relaxivities. Polyethyleneoxide–polyethylenecarbonate derivatives of *p*-tert-butylphenols are introduced as amphiphiles for efficient hydrophilization of oleate-stabilized iron oxide nanoparticles. The obtained results reveal the easy variation of the synthetic conditions as the route to switch from the recoating to the dissolution of the oleate-stabilized iron-oxide nanoparticles. The length of ethylenecarbonate chains is highlighted as the factor affecting the transverse relaxivity (R_2) and the colloid properties of the synthesized colloids, evaluated from DLS data. The complex ability of ethylenecarbonate chains is the reason for loading of the synthesized colloids by Gd(III) ions in aqueous dispersions at specific conditions. These conditions are introduced herein as a route of gaining in longitudinal relaxivity (R_1) and tuning R_2/R_1 ratio.
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1. Introduction

The hydrophilization of iron oxide cores by water soluble polymers with repeating ethyleneoxide moieties has gained a great deal of attention during recent decades, since it provides a facile way to synthesize functional nanomaterials. For example, the transverse relaxivities of iron oxide cores decorated by PEGs and polyelectrolytes are commonly greater than for those coated by silica [1,2]. The biocompatibility of PEGs and polyelectrolytes is one more argument for the non-covalent hydrophilization of iron oxide nanoparticles (IONs) versus silica coating.

The complex ability of polyelectrolyte-based hydrophilic coating towards metal ions along with magnetic properties of iron oxide cores makes the polyelectrolyte-coated IONs efficient extractants of metal ions with easy magnetic phase separation [3]. The hydrophilic stabilization of IONs by PEGs or so-called PEGylation provides the route for obtaining dual-mode contrast agents through the doping of both iron oxide and gadolinium oxide nanoparticles into hydrophilic colloids [4].

Dual-mode contrast agents are a top of current interest today due to their impact in diagnosis and therapy of damaged organs or tissues [5,6]. This impact derives from shortcomings of both gadolinium chelates and iron oxide nanoparticles in an imaging of tissues through shortening of transverse ($1/T_2$) or longitudinal ($1/T_1$) relaxation rates of water protons when exposed to the strong external magnetic field [7–11]. In order to boost up sensitivity, biocompatibility and avoid undesirable magnetic susceptibility effects new contrast agents which simultaneously carry T_2 and T_1 function are in great demand. The literature data on encapsulation of both iron oxide and Gd(III) ions into hydrophilic nanoparticles reveal the influence of two main factors, which are separation between T_1 and T_2 bearing components and R_2/R_1 ratio [12]. The optimal separation between T_1 and T_2 components should be on a distance about 20 nm, which can be obtained by the proper morphology of nanomaterial [12]. R_2/R_1 can be modified by an optimization of Fe:Gd molar ratio. From the viewpoint of the above mentioned factors non-covalent decoration of IONs by hydrophilic coating built through self-organized amphiphilic molecules can be considered as promising

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