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Composite magnetic particles: 2. Encapsulation of iron oxide by surfactant-free emulsion polymerization

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Abstract

This is a second paper in the series concerning the synthesis and characterization of composite polymeric particles with encapsulated magnetic iron oxide and bearing reactive β-diketone groups on the surface. Composite particles have been prepared by two-step method in which first step requires preparation of the iron oxide nano-particles and during second step iron oxide was encapsulated into formed poly(styrene/acetoacetoxyethyl methacrylate) (PS-AAEM) particles directly during polymerization process. It has been found that the modification of the iron oxide nano-particle surface with sodium oleate improves significantly the encapsulation during polymerization process. This procedure gives a possibility to obtain composite particles with raspberry morphology and both the particle size and iron oxide content can be varied. Change of monomer to iron oxide ratio gives a possibility to change effectively the morphology of hybrid particles, however, polydispersity of composite particles increases at higher content of magnetic particles in the system. Variation of AAEM concentration in reaction mixture at constant iron oxide particles concentration gives a possibility to control the particle size of formed hybrid microspheres. Composite particles were characterized by dynamic light scattering and electron microscopy (SEM) with respect to their particle size and morphology of the surface layer. X-ray diffraction (XRD) and magnetization measurements indicate presence of maghemite (γ-Fe_2O_3) in composite particles.

Keywords: Iron oxide; Hybrid latex particles

1. Introduction

There is a considerable interest in preparation of particles which can be manipulated in different systems by external stimuli such as thermal, electric or magnetic field. Polymeric particles can be easily prepared and their size, morphology and surface groups can be varied in the broad range. However, conventional polymers cannot provide some special properties like, for example magnetic response. Therefore, incorporation of magnetic iron oxides in polymeric particles can be an interesting route for preparation of hybrid particles which can provide this interesting feature.

Various strategies have been proposed for synthesis of magnetic polymer particles [1]. Ugelstad and co-workers developed a novel method based on a two-step swelling technique and successfully prepared monodisperse magnetic microspheres [2,3].

Recently the layer-by-layer deposition technique was developed by Caruso and co-workers [4,5] to prepare functionalized microcapsules from oppositely charged polyelectrolytes with loaded magnetite.

The stepwise heterocoagulation method has been successfully used by Furusawa et al. [6] and Sauzedde et al. [7,8] to form magnetic particles by coagulation of two different colloids one of them being magnetic. Sauzedde et al. [7,8] developed a three-step procedure which requires (a) synthesis of different seed particles (polystyrene, poly (styrene/*N*-isopropylacrylamide) and poly (*N*-isopropylacrylamide), (b) adsorption of magnetic nano-particles on the seed particle surface, and finally (c) seed precipitation polymerization of *N*-isopropylacrylamide. Authors obtain

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superparamagnetic, hydrophilic microspheres with various dimensions and magnetite contents. Dresco et al. [9] reported preparation of magnetic polymeric nano-particles by synthesis of magnetite core and polymeric shell in a single inverse microemulsion. The polymerization of methacrylic acid, hydroxyethyl methacrylate and cross-linker lead to formation of stable hydrophilic polymeric shell. Recently Gu et al. [10] reported a novel method for preparation of magnetic latex particles. In this approach coating of polymer particles with surface-modified magnetic particles with silane reagents occurs during soap-free emulsion polymerization. Condensation of SiOH groups on the magnetic and polymeric particles followed by polymerization of vinyl bonds lead to formation of hybrid particles with different morphologies. Elaissari et al. [11] designed a new strategy for preparation of magnetic particles requiring no final polymerization step. In this approach small film-forming positively charged nano-particles coagulate on the surface of negatively charged magnetic particles and form a polymeric shell when heated above their T_g. In this way also fluorescent particles have been incorporated into polymeric shell and hybrid particles with high iron oxide content have been obtained.

In previous paper [12], we described synthesis of PS-AAEM polymeric particles by surfactant-free emulsion polymerization. Monodisperse latex articles functionalized with β-diketone groups have been obtained and characterized. Since β-diketone groups are capable to chelate effectively metal ions, obtained polymeric particles have been used as templates for iron oxide deposition what leads to formation of hybrid core-shell composites. Present paper summarises the results about formation of hybrid particles *in situ* by encapsulation of pre-formed iron oxide nano-particles during surfactant-free emulsion polymerization of styrene (ST) and acetoacetoxyethyl methacrylate (AAEM).

2. Experimental part

2.1. Materials

Styrene (ST) (from Fluka) and acetoacetoxyethyl methacrylate (97%) (AAEM) (from Aldrich) were purified by conventional methods and then vacuum distilled under nitrogen. Sodium peroxydisulfate (97%) (SPDS) and 2,2′-azobis(2-methylpropyonamidine) dihydrochloride (97%) (AMPA), iron (III) chloride ($FeCl_3$), iron (II) chloride ($FeCl_2$), and sodium oleate were received from Aldrich and used as commercially available. Ammonium hydroxide (NH_4OH) in form of 40% water solution was obtained from Fluka. Distilled water was employed as polymerization medium.

2.2. Synthesis of iron oxide particles

Solutions of $FeCl_2$ and $FeCl_3$ were prepared in separate flasks and added to stirred dispersion under nitrogen blanket (molar ratio $FeCl_3$:$FeCl_2$ was kept constant at 2:1). Water solution of NH_4OH was added drop-wise to start iron oxide formation process. Immediately after base addition solution became dark-brown indicating that iron oxide has been formed in the system. After 30 min formed composite particles were removed from reaction vessel and cleaned by precipitation to remove all by-products. Magnetic nano-particles were washed with 0.01 M HCl solution. Magnetic dispersion with HCl solution was centrifuged (Universal 16 A) at a speed of 3000 U/min for 25 min to precipitate the particles. This procedure was repeated for four times. After that precipitated magnetic particles were cleaned with distilled water. Then calculated amount of sodium oleate was added to the required amount of magnetic dispersion (15 mg Na-oleate in 50 ml of 1.1 mg/ml magnetic dispersion, keeping the ratio constant at 1:1). Then the dispersion was heated to 80 °C for 5 min and finally sonified for another 5 min.

2.3. Synthesis of PS/AAEM/Iron oxide particles

Double-wall glass reactor equipped with stirrer and reflux condenser was purged with nitrogen. Appropriate amounts of iron oxide dispersion (from 0.92 to 9.2 g) were diluted with water to keep the total water amount 20 g and then ST (1.33 g) and AAEM (0.07 g, 5% to ST) were added into reactor and stirred at room temperature. After 10 min temperature was increased to 70 °C and water solution of initiator (0.07 g in 2 g water) was added to start the polymerization process.

2.4. Analytical methods

2.4.1. Particle size analysis

A commercial laser light scattering (LLS) spectrometer (ALV/DLS/SLS-5000) equipped with an ALV-5000/EPP multiple digital time correlator and laser goniometer system ALV/CGS-8F S/N 025 was used with a helium-neon laser (Uniphase 1145P, output power of 22 mW and wavelength of 632.8 nm) as the light source.

In dynamic LLS, the intensity-intensity-time correlation function $g_2(q,t)$ in the self-beating mode was measured and can be expressed by the Siegert relation:

$$g_2(q,t) = A(1 + \beta|g_1(q,t)|^2) \tag{1}$$

where t is the decay time, A is a measured baseline, β is the coherence factor, and $g_1(q,t)$ is the normalized first-order electric field time correlation function and $g_1(q,t)$ is related to the measured relaxation rate Γ:

$$g_1(q,t) = G(\Gamma)\exp(-\Gamma t)d\Gamma \tag{2}$$

A line-width distribution $G(\Gamma)$ can be obtained from the Laplace inversion of $g_1(t)$ (CONTIN procedure) [10]. For a pure diffusive relaxation, Γ is related to the translational