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Synthesis and characterization of anisotropic magnetic hydrogels

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ABSTRACT

Multiresponsive hydrogels are an interesting new class of materials. They offer the advantage, that they respond to different stimuli like temperature, pH and magnetic fields. By this they can change their properties which makes the hydrogels ideal candidates for many applications in the technical as well as medical field. Here we present the synthesis and characterization of hydrogels - micro- as well as macrogels - which consist of an iron oxide core, varying in phase and morphology, embedded in a thermoresponsive polymer, consisting of poly N-isopropylacrylamide. By using dynamic light scattering we investigated the thermoresponsive properties. In addition we were able to follow the formation of the macrogel by monitoring the shear viscosity.

1. Introduction

A polymer network extensively swollen with water is generally called a hydrogel [1]. The polymer network of the hydrogel consists of one or more monomer species which are cross-linked to form a network that is able to swell and retain a significant amount of water without being dissolved by water [1]. Hydrogels are of interest because they have possible applications in many areas including microfluidics [2], medicine [3–5] and waste water treatment [6]. Hydrogels are suitable for those applications because of their ability to swell and shrink based on their environment or as a response to external stimuli, especially changes in the pH of the surrounding solution [7], to gases in their environment [8] and to temperature [9]. Poly-N-isopropylacrylamide (pNipam) is the most studied thermoresponsive polymer because of its lower critical solution temperature (LCST) around the human body temperature and corresponding swelling/shrinking properties in aqueous media [10–12].

Magnetic particles can be manipulated by an alternating current (AC) field [13]. Hydrogels combined with magnetic particles can additionally switch their properties, like pore-size, overall size and water-uptake by a magnetic field [14]. If for example an AC field is applied while magnetic particles are embedded in a thermoresponsive hydrogel, they heat the surrounding hydrogel and can even cause the polymer chains to collapse [15].

Anisotropic particles display a higher coercitivity field strength [16], so a magnetic field has a stronger influence on them. Since the particles react to a magnetic field, they align along the field lines [17].

The goal of this work was to connect the properties of a thermoresponsive hydrogel to those of anisotropic magnetic particles. Here we use anisotropic magnetic particles consisting of hematite and magnetite and embed them into pNipam. Compared to other studies we not only prepare microgel particles, we also cross-link those to a pNipam macrogel. The macrogel formation has been studied by its rheological properties. The synthesis process can be transferred to different magnetic particles in the same manner.

2. Materials and methods

$NaH_2PO_4 \cdot 2H_2O$ (99.5%), $FeCl_3 \cdot 6H_2O$ (97%), N_2H_4 35% solution in water, 3-(trimethoxysilyl)propyl methacrylate (TPM) (98%), allylamine (AA) (≥99%), glutaraldehyde in solution (GA) (50%) were obtained from Sigma Aldrich. N-Isopropylacrylamide (Nipam) (99%), N,N methylen-bis-acrylamide (BIS) (96%) were aquired from Acros Organics. Sodium lauryl sulfate (SDS) (99%), poly-vinylpyrollidone (40k g/mol) (PVP) (100%) were bought from Carl Roth. Sodiumsulfite (100%) and potassium peroxodisulfate (KPS) (≥99%), ammonium iron sulfate hexahydrate (AIS) (100%) were bought from Merck. All reagents were used as received without further purification.

Transmission electron microscopy (TEM) images were taken, using a JEOL JEM-1011 microscope with an acceleration voltage of 200 kV.

X-ray diffraction (XRD) was measured using a Philips X′pert Pro MPD diffractometer.

Dynamic light scattering (DLS) was done with a ALV/CGS-3 Compact goniometer system at a wavelength of 532 nm, with an attached ALS/LSE-5004 light scattering electronics and multiple tau digital correlator.

Magnetization measurements were performed with a vibrating sample magnetometer (Princeton applied research model 155), to-

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gether with a Bruker Forschungsmagnet B-E 25 C8U. The magnetization was measured up to a field strength of 1.1 T.

For the rheological measurements a modular compact rheometer MCR502 by Anton Paar was used. As sample environment a cone plate system, with a diameter of d=50 mm was used which was placed in a closed chamber and the temperature was kept constant by a Peltier temperature control.

2.1. Hematite particle synthesis

Hematite particles were synthesized in a hydrothermal reactor by hydrolysis of ferric chloride after a modified approach of Ozaki [18]. 0.01 M $FeCl_3$ solution were heated up to 100 °C in an autoclave at 1.5 bar. After eight days the ferric chloride turned into reddish hematite. The reaction solution was filtrated and washed with water.

2.2. Magnetite particle synthesis

In a first step β-FeOOH particles were synthesized similar to the works of Sugimoto and Muramatsu [19]. A 0.02 M $FeCl_3$ and 0.002 M NaH_2PO_4 solution was heated to 80 °C for 48 h and later dialyzed for 7 days. The solvent was removed with a rotary evaporator.

Similar to the approach of Peng et al. [20] 0.2 M β-FeOOH was reduced with 0.016 M N_2H_4 in aqueous solution. The dispersion was put into a teflon lined stainless steel autoclave and heated to 150 °C for 24 h. The resulting black precipitate was washed three times with water and ethanol.

2.3. Encapsulation of the magnetite/hematite into a hydrogel

For the silica coating a modified Stöber process supported by PVP was employed [21]. Additionally after 24 h TPM was added with a small amount of ammonium hydroxide and stirred for further 24 h. The ammonium hydroxide was removed after the synthesis and the particles were purified by dialysis against ethanol.

The polymer shell around the silica particles was synthesized by a free radical emulsion polymerization [21]. A dilute solution of the iron oxide particles with a silica shell has been stirred for 30 min with SDS and sodium sulfite under constant nitrogen flow. The solution was heated to 60 °C and KPS was added together with one crystal of AIS. The polymerization started by pumping an ethanol solution with Nipam and BIS. After another 3 h an ethanol solution with Nipam and AA was added. The solution was stirred for another 20 h under nitrogen at 60 °C [22]. When the reaction has finished the solution was dialyzed for 8 days.

In a further step this microgel (~16 wt% solution in water) was cross-linked to a macrogel by addition of GA [22].

3. Results and discussion

In a first step we synthesized hematite particles and coated them with a silica shell. The phase of hematite was confirmed by XRD measurements. From TEM images the half widths of the hematite cubes were determined to 27.2 ± 5.2 nm without and about 36.7 ± 8.1 nm with silica coating (Fig. 1).

The vinyl group introduced by the addition of TPM provides the starting point for the free radical emulsion polymerization of Nipam. The pNipam polymer chains are cross-linked by BIS. In addition AA is introduced to provide an amine function on the surface of the microgel particles.

The swelling and shrinking behavior was monitored by DLS (Fig. 2). The swollen polymer has a hydrodynamic radius of about ~200 nm while the collapsed microgel has a radius of ~70 nm. There is a small hysteresis between heating and cooling. The restored gel does only reach the dimensions of the as synthesized gel (180 nm). The LCST is at 33.5 °C for the heating process and at 33.0 °C for the cooling process. Normally pNipam polymers become insoluble above their LCST and precipitate because their chains turn hydrophobic. However, due to the surface charges provided by the choice of initiator, the microgel particles remain stable in dispersion, the fluid just turns white and turbid.

In the last step of the synthesis, the microgel particles are cross linked by GA. The amine groups react with the aldehyde groups and form an amide bond so a covalently bound polymer network is formed. This transforms the microgel, previously dispersed in water, into a macrogel, a solid material still containing water. The hydrogel preserves the thermoresponsive properties of the microgel. The coil to globule transition at the LCST is still visible by the color change of the macrogel. At low temperature the macrogel is swollen with water and shows a clear orange color whereas above the LCST the macrogel turns turbid and white like the microgel dispersion.

The gelation process was studied while applying constant shear stress of about 10 s^{-1} (Fig. 3). For this the sample was mixed shortly with glutaraldehyde and directly inserted between the gap of the cone plate of the rheometer and shear stress was applied. At the beginning the viscosity was the same as for the microgel without GA at 20 and 30 °C respectively (data not shown here). After about 2 h at 30 °C and 6 h at 20 °C the gelation process starts which is visible by a dramatic exponential increase of the viscosity leading to highly viscous macrogels with a viscosity of about 10^4 mPas. This is an increase of the

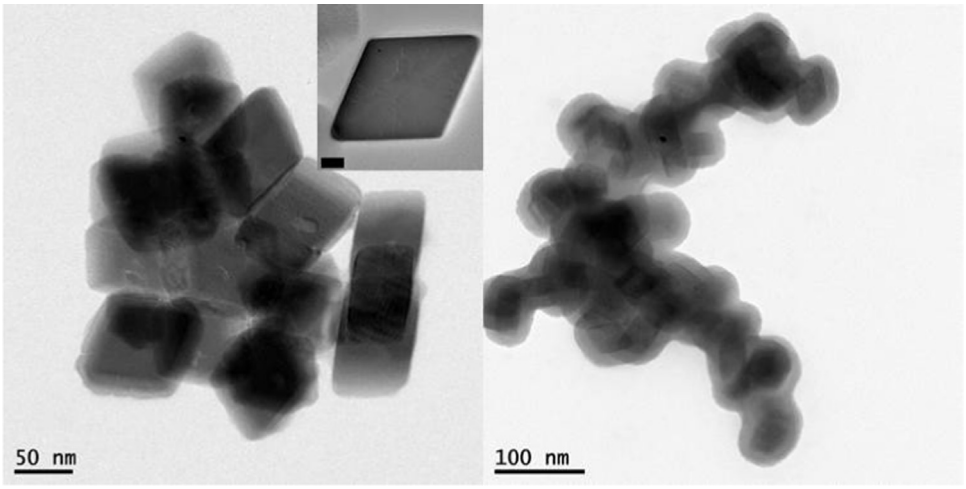

Fig. 1. Shape of the hematite particles: Hematite particles directly after the synthesis (left hand side) and after silica coating (right hand side). The inlet shows the typical cubic shape of a single particle. The scale bar in the inlet shows 10 nm.

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