



## Betaine microgel preparation from 2-(methacryloyloxy) ethyl dimethyl (3-sulfopropyl) ammonium hydroxide and its use as a catalyst system



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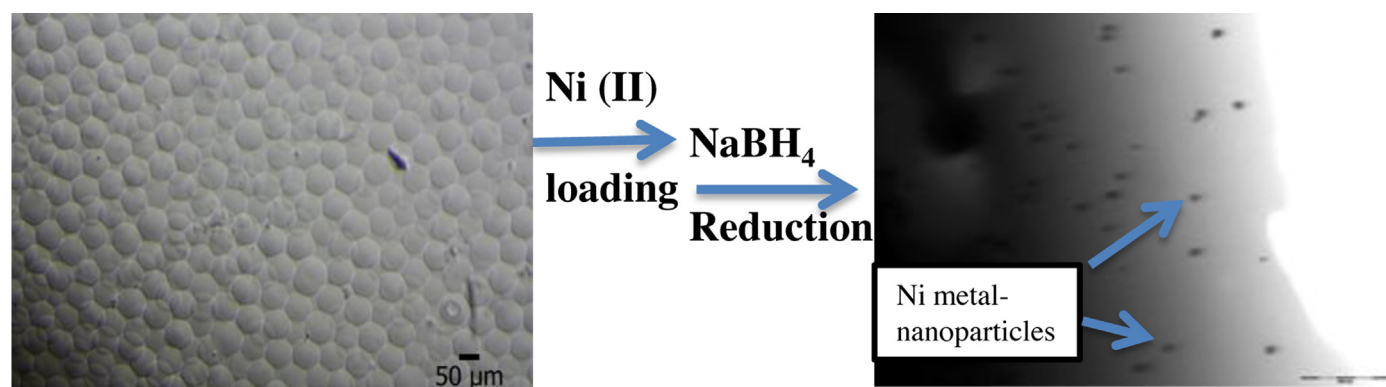
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### GRAPHICAL ABSTRACT



### Swollen Betaine Microgels

### HIGHLIGHTS

- Poly betaine microgel via inverse suspension polymerization.
- Well distributed Ni nanoparticles are prepared within microgels of betaine polymers.
- Highly active p(MEDSAH)-Ni composite catalyst for 4-NP reduction.
- Environmental application of zwitterionic microgel as template and catalyst.

### ARTICLE INFO

#### Article history:

Received 27 June 2015

Received in revised form 6 September 2015

Accepted 11 September 2015

Available online 14 September 2015

### ABSTRACT

We demonstrate the synthesis of poly(sulfobetain methacrylate) (p(SBMA)) hydrogels of micro dimensions by inverse suspension polymerization of a zwitterionic monomer 2-(methacryloyloxy) ethyl dimethyl (3-sulfopropyl) ammonium hydroxide (SBMA). The prepared microgels were used as microreactors for the synthesis of nickel (Ni) nanoparticles by *in situ* reduction of Ni (II) loaded into microgels

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**Keywords:**

Hydrogel/Microgel betaine  
Zwitterionic microgel  
Ni nanoparticles  
Catalysis

from an aqueous medium. The prepared microgels and microgel metal nanoparticle composites were characterized by Fourier Transformation Infrared (FT-IR) Spectroscopy, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Thermal properties of the microgels were studied by thermal gravimetric analysis (TGA). The amount of Ni nanoparticles generated within the microgels was determined by Atomic Absorption Spectroscopy (AAS) after dissolving the Ni nanoparticles to form Ni (II) ions by treating with concentrated hydrochloric acid (5 M HCl). The prepared composites were used as catalysts for the reduction of nitro aromatic compounds such as 4-nitrophenol (4-NP), 2-nitrophenol (2-NP) and 4-nitroaniline (4-NA) and excellent catalytic performances were observed. The effects of temperature and amount of catalyst were also evaluated. A mild activation energy in comparison to the literature was calculated as 35.64 kJ/mol, and very high  $k_{app}$  value of 0.42 min<sup>-1</sup> as a function of temperature was estimated for the reduction of 4-NP catalyzed by p(SBMA)-Ni composite catalyst system.

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## 1. Introduction

Ampholyte hydrogels are three dimensional cross-linked polymeric networks that contain both positively and negatively charged groups in their chemical structure. They can be prepared either by copolymerizing anionic and cationic monomers forming positive and negative charges in different polymer repeating units (polyampholytes) [1–4], or by polymerization of a zwitterionic monomer to obtain anionic and cationic charges in the same repeating units (polybetaines) [5,6]. Sulfobetaines are an important class of zwitterionic structures that contain a quaternary ammonium and a sulfonate group. Due to the presence of these positively and negatively charged groups within the same repeating units, sulfobetaine (with neutral monomers) microgels that are prepared from sulfobetaine monomers can maintain a constant near net-zero charge irrespective of the pH of the medium [7]. The coexistence of a positive and a negative charge on the same repeating unit creates a strong electrostatic interaction with water molecules resulting in the formation of a hydration layer at the material surface [8–10]. This strong hydration layer introduces super low fouling properties in zwitterionic materials. Therefore, zwitterionic materials, specifically poly sulfobetaines have gained much attention due to their very low biofouling properties [11–17]. It has been reported that poly(sulfobetaine methacrylate) (p(SBMA)) hydrogels are highly resistant to nonspecific protein adsorption and cell adhesion *in vitro* and *in vivo* [12–14,17,18]. Inhibition of bacterial adhesion by self-assembled monolayers of p(SBMA) has been demonstrated by Cheng et al., [15]. Although the properties of p(SBMA) polymers and their macroscopic and copolymeric gels have been studied [19,20], there is no report on the synthesis and applications of zwitterionic hydrogels in micro dimensions such as microgels. Moreover, biological applications such as inhibition of bacterial adhesion and low fouling properties of p(SBMA) hydrogels have been studied up to now. However, p(SBMA) hydrogels have never been used as templates for the *in situ* synthesis of metal nanoparticles, whereas polymer hydrogels can act as templates for the *in situ* synthesis of metal nanoparticles with predetermined dimensions by changing the composition and the structure of microgels [21]. So the use of zwitterionic microgels as templates for the synthesis of metal nanoparticles can provide a new platform as template for the preparation and tuning of catalytic properties of metal nanoparticles. In comparison to bulk hydrogels, microgels can offer greater surface area that is favorable to metal ion-trapping and then act as a microreactor in catalytic applications. Due to the ability of microgels to absorb large amounts of water without any structural breakdown, microgels can be used as microreactors in the synthesis of different metal nanoparticles within their network and the aggregation of the prepared metal nanoparticles can be prevented due to the polymeric chains and the functional groups in the microgel networks that can act as capping agents [22]. Because

of these advantages, microgels are widely used as microreactors for the *in situ* synthesis of metal nanoparticles and then the prepared microgel metal nanoparticle composites are used as catalysts for various reactions. The use of microgels as microreactors is gaining worldwide interest as this is a very versatile technique for the synthesis of various metal nanoparticles of desirable shapes and sizes that can be produced by controlling the composition of microgel networks as well as the reducing agents. The shape, size, composition, and architecture of microgel particles can also be controlled by the polymerization techniques [23]. Additionally, the prepared microgel metal nanoparticle composites can be used as catalysts directly, and their catalytic properties can be tuned by changing the chemical composition of microgels and metal ions. Moreover, the microgel behavior in response to external stimuli, such as temperature, pH, magnetic field, etc., provides another important benefit in the design of advanced material systems [24,25]. Previously, the use of cationic, anionic and polyampholyte microgels as microreactors in the synthesis of different metal nanoparticles have been reported by our research group [25–27]. In the present study, we have synthesized a novel zwitterionic microgel consisting of poly 2-(methacryloyloxy) ethyl] dimethyl (3-sulfopropyl) ammonium hydroxide (also known as p(SBMA)), and then used this as template for the *in situ* synthesis of Ni nanoparticles. The catalytic properties of the prepared composites were investigated for the reduction of nitro aromatic compounds such as 4-nitrophenol (4-NP), 2-nitrophenol (2-NP) and 4-nitroaniline (4-NA). Comparison of catalytic efficiency of the prepared composite catalysts for various nitro compounds was completed. The effect of temperature on the catalytic activity was also evaluated to calculate activation energy, and other thermodynamic parameters such as activation enthalpy change ( $\Delta H^\ddagger$ ), activation entropy change ( $\Delta S^\ddagger$ ) and Gibb's free energy of activation ( $\Delta G^\ddagger$ ).

## 2. Experimental

### 2.1. Materials

The monomer, 2-(methacryloyloxy) ethyl] dimethyl (3-sulfopropyl) ammonium hydroxide (SBMA, 97%, Sigma–Aldrich), the crosslinker N,N' methylenebisacrylamide (MBA 99%, Acros), the initiator ammonium persulfate (APS, Aldrich), and the accelerator N,N,N',N'-tetramethylethylenediamine (TEMED, Merck) were used as received. Sorbitane monooleate (SPAN®80, Fluka) was used as a surfactant. Gasoline (95 octanes) was used as solvent and procured from a local gas station. Nickel (II) chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O, 97%, Riedel-de Haën) was used as metal ion source, and sodium borohydride (NaBH<sub>4</sub>, 98% Aldrich) was used as reducing agent for metal nanoparticle preparation. Aromatic nitro compounds of 2-nitrophenol (2-NP, 99% Acros), 4-nitrophenol (4-NP, 99% Acros) and 4-nitroaniline (4-NA, 99% Sigma) were used

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