



Cubic polyhedral oligomeric silsesquioxane nano-cross-linked hybrid hydrogels: Synthesis, characterization, swelling and dye adsorption properties



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ABSTRACT

In this study, a new series of hybrid hydrogels based on poly(*N*-isopropyl acrylamide-*co*-itaconic acid) containing octavinyl polyhedral oligomeric silsesquioxane (OV-POSS) nontoxic cross-linker with different feed ratio were fabricated via free radical copolymerization. The resulted hydrogels were characterized by FT-IR, SEM, XRD and TGA analysis. Various parameters such as time, temperature, pH and salt effects were investigated on the swelling as well as dye removal properties of hybrid hydrogels. The adsorption experiments showed that the maximum adsorption capacity accrued at pH 11 for methylene blue. Adsorption kinetics was elucidated by both pseudo-first-order and pseudo-second-order kinetic models under different conditions. Also, adsorption isotherm of the adsorption of methylene blue on poly(NIPAM-*co*-IA)/POSS₈ adsorbent was investigated using Langmuir, Freundlich, Redlich–Peterson and Sips models, in which the experimental data were fitted well with Langmuir, model.

1. Introduction

Over the past years, surrounding environment exposure to the toxic organic dyes contaminated effluents from modern industries has risen exponentially. Methylene blue (MB) is one of the most important organic dyes, which widely used in textile industries [1], and can cause some harmful effects such as increased heart rate, shock, tissue necrosis, jaundice and eye burns [2]. Therefore, it is vital to develop various physicochemical and biochemical treatment techniques in order to remove these types pollutants from wastewater [3,4]. Apart from the above mentioned treatment processes, adsorption might be considered as a promising technique because it is not only simple for operation but also can produce high-quality water with low cost [5]. Nowadays, a broad range of materials have been reported as adsorbents [6–8]. It is worth to mention that the most traditional adsorbents are either very expensive or difficult to be recovered or non-degradable. To solve the aforementioned shortcomings, design and synthesis of novel adsorbents still is required with high adsorption efficiency. And most importantly, the adsorbents should be accepted from environmental point of view.

Hydrogels are highly swollen cross-linked hydrophilic polymer networks which can absorb large amount of water without being dissolved [9]. In addition, the type of monomers as well as the degree of

crosslinking can affect the swelling ability of hydrogels with water. Recently, stimuli responsive hydrogels gained tremendous attention because of their potential applications in bioseparations [10], biomedicine [11], water purification [12] and agriculture [13]. Smart hydrogels containing basic or acidic pendant functional groups such as OH, CONH₂, COOH and SO₃H, exhibit remarkable changes in their volume and mechanical properties in response to a change of external environment conditions such as pH [14], temperature [15], light [16] and magnetic field [17]. Among stimuli responsive hydrogels, temperature and pH dual responsive hydrogels have been frequently investigated because pH and temperature are two substantial environmental parameters in biomedical and other fields [18,19]. Poly(*N*-isopropyl acrylamide) (PNIPAM) is well-known as the best thermo-sensitive polymeric network due to its exhibiting a lower critical solution temperature (LCST) at about 32–34 °C. When the PNIPAM polymeric gel is heated above the LCST, abrupt changes are occurred in its volume and dehydrated to collapse quickly. As the temperature is decreased below LCST, the PNIPAM polymeric gel is swollen in water [20]. The LCST values of PNIPAM based polymeric materials can be tuned by copolymerization with hydrophilic and hydrophobic comonomers [21]. Monoprotic acids namely acrylic and methacrylic acid had been extensively used as important comonomers in the copolymerization with *N*-isopropyl acrylamide (NIPAM) [22]. Nowadays, itaconic acid (IA) as

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diprotic acid has been considered as suitable alternative for substitution of monoprotic acids due to its easy copolymerization, high hydrophilicity and biocompatibility [23]. Additionally, IA has two carboxylic acid groups with different pK_a which not only provides good pH sensitivity but also bring additional ability of chelate formation under specific conditions [23]. Combination of pH-sensitive and temperature-sensitive comonomers enables a facile control over the copolymer phase property, resulting in multifunctional intelligent materials such as poly (NIPAM-co-IA) copolymeric hydrogels.

Generally, in order to prepare chemically crosslinked hydrogels, crosslinkers such as *N,N*-methylene-bis-acrylamide (MBAA), ethylene-glycol dimethyl-acrylate, tetra-ethyleneglycol dimethyl-acrylate or tri-propyleneglycol diacrylate are often utilized, which are usually toxic and the as-prepared hydrogels are brittle and nonbiodegradable [24,25]. Using inorganic components as nanofiller in the copolymerization process to prepare new smart polymeric networks is feasible alternative method overcoming the aforementioned problems, leading to provide organic-inorganic nanocomposite hydrogels [26]. Polyhedral oligomeric silsesquioxanes (POSS) as the smallest silica particles are rigid molecules of nanoscale 3D-dimensions (1–3 nm) with the empirical chemical formula $(RSiO_{1.5})_n$, where $n = 4, 6, 8, 10$ and R can be a range of active or inert organic groups [27–29]. Among them, octa-silsesquioxane (T_8 -POSS) with its cubic inorganic silica core and eight pedant organic groups has been investigated widely [30]. POSS molecule and its derivatives consist of unique properties including cubic-symmetrical, well-defined, nanometer-sized structures in which enables scholars worldwide to fabricate a lot of new hybrid organic-inorganic materials [31–32]. Typically, POSS nanoparticles can be incorporated into the polymeric structures via copolymerization, grafting, cross-linking or simple blending methods in order to enhance significantly their physical and mechanical properties [33,34].

Cage-like octavinyl polyhedral oligomeric silsesquioxane (OV-POSS) with eight vinyl groups on the corners is one of the most important POSS compounds and can be utilized as an efficient, non-toxic and cytocompatible cross-linker in the preparation of organic-inorganic polymer networks [35,36].

There is a few reports on the preparation of organic-inorganic hydrogels using POSS as cross-linker. Mu and Zheng reported octa(propylglycidyl ether) POSS as cross-linker for the preparation of PNIPAM hydrogel, and investigated its temperature-responsive behavior [37]. In another report Zhang et al. developed a temperature and pH dual-responsive hybrid hydrogel by copolymerization of 2-(dimethylamino) ethyl methacrylate and NIPAM, cross-linked with OV-POSS for drug releasing application [38]. Very recently, we have reported OV-POSS as cross-linker for the copolymerization of acrylamide and itaconic acid, in which hybrid nano-composites were obtained, indicating a high ability to adsorb crystal violet dye from aqueous solutions [39]. To the best of our knowledge, the preparation of OV-POSS nano-cross-linked poly (NIPAM-co-IA) hybrid hydrogels has not been reported to date.

In this article, the fabrication of a novel OV-POSS nano-cross-linked hybrid hydrogels based on NIPAM and IA in the absence of MBAA or other toxic cross-linkers via simple free radical copolymerization was reported. The resultant hybrid hydrogels were assigned as poly(NIPAM-co-IA)/OV-POSS_n where $n = 4, 6, 8, 10$ and 12 exhibiting the OV-POSS

wt% and characterized using FT-IR, X-ray diffraction (XRD), thermal gravimetric analysis (TGA), scanning electron microscopy (SEM) and EDX analysis. In addition, the effect of various parameters such as pH, contact time, salt, and temperature on the swelling profile of hybrid hydrogel as well as its dye removal ability have been systematically investigated. Due to the existence of carboxylate groups, hydrogels could act as adsorbent for cationic dyes. In this context, we chose MB as a model of cationic dyes in order to investigate the ability of the synthesized hydrogels for the removal of cationic dyes from aqueous solutions, however, MB itself is one of the toxic cationic dyes and its removal from wastewater is of interest.

2. Experimental

2.1. Materials

N-Isopropylacrylamide (NIPAM), itaconic acid (IA) and methylene blue (MB) were purchased from Sigma-Aldrich. Octavinyl polyhedral oligomeric silsesquioxane (OV-POSS) and 2,2'-azobisisobutyronitrile (AIBN) were purchased from Merck (Schuchardt, Germany). AIBN was recrystallized from ethanol prior to use. Tetrahydrofuran (THF) was dried on Na/benzophenone under a nitrogen atmosphere immediately before use. All other reagents and solvents were of analytical grade and used as received.

2.2. Preparation of hybrid hydrogels

All copolymerization reactions were carried out in sealed 0.5×10 cm (diameter \times length) plastic tubes which were under nitrogen gas using vacuum-line system for 40 min to wipe out dissolved oxygen. The poly(NIPAM-co-IA)/OV-POSS_n hybrid hydrogels were synthesized via one-pot free radical copolymerization method. Taking poly(NIPAM-co-IA)/OV-POSS₈ as an example, the hybrid hydrogel was fabricated as follows: NIPAM (3.20 g, 28 mmol), IA (0.80 g, 6 mmol), OV-POSS (0.32 g, 0.43 mmol) and AIBN (0.04 g, 0.24 mmol) were fed into a plastic tube containing 8 mL THF and dissolved at room temperature. The copolymerization was started after placing the tube in an oil bath at 70 °C for 24 h.

Then in order to remove unreacted monomers, cross-linker and linear polymers, the resultant hydrogel was immersed in deionized water (DI water) for 6 h and THF for 6 h alternatively (three times) at room temperature. The formed hybrid hydrogel was allowed for drying in a vacuum oven at 50 °C for 20 h. The physical properties of the series of obtained hybrid hydrogels were summarized in Table 1.

2.3. Instruments

The chemical nature of the obtained hybrid hydrogels was examined with a Win-Bomem, version 3.04 Galatic Industries Corporation spectrometer over the range of 400–4000 cm^{-1} by spectroscopic grade KBr powder at room temperature. ^1H NMR spectra were recorded in DMSO- d_6 as solvent on a Bruker 300 MHz instrument. Wide angle X-ray powder diffraction spectrum of samples were collected at room temperature with a Bruker D8 Advance diffractometer using a Cu K α

Table 1
Physical properties of OV-POSS based hybrid hydrogels.

Sample	OV-POSS (wt%)	Color & appearance	Solubility in water
Poly(NIPAM-co-IA)	0	White powders	Soluble
Poly(NIPAM-co-IA)/OV-POSS ₄	4	White glassy gel	Soluble after 3 h
Poly(NIPAM-co-IA)/OV-POSS ₆	6	White glassy gel	Soluble after 5 h
Poly(NIPAM-co-IA)/OV-POSS ₈	8	White glassy gel	Insoluble and swelled
Poly(NIPAM-co-IA)/OV-POSS ₁₀	10	White opaque gel	Insoluble and swelled
Poly(NIPAM-co-IA)/OV-POSS ₁₂	12	White opaque gel	Insoluble and swelled

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