



# Hydrolytically degradable POSS-PEG hybrid hydrogels prepared in aqueous phase with tunable mechanical properties, swelling ratio and degradation rate

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## ABSTRACT

A series of hydrolytically degradable polyhedral oligomeric silsesquioxanes (POSS)-poly(ethylene glycol) (PEG) hybrid hydrogels were prepared by covalently grafting hydrophobic POSS onto hydrophilic 4-arm-PEG-maleimide to form an amphiphatic precursor and further cross-linking with hydrolytically PEG-diester-dithiol via Michael-type addition. The process to form hydrogels was in aqueous phase completely, which is free of metal catalyst, UV irradiation, and organic solvents. In addition, POSS as enhanced agents, only small amounts are needed to cause significant changes in hydrogels properties due to the special surface properties and high mechanical stability of the nanosize particles. Experimental results showed that by increasing the mass fraction of POSS from 0% to 4%, the storage modulus ( $G'$ ) of the hybrid hydrogels have observably increased from 250 Pa to 1800 Pa. Furthermore, the hybrid hydrogels exhibited a good water absorption capacity and they can be degraded by hydrolysis. The swelling ratio of the hybrid hydrogels decreased with the increase of the POSS content and the microstructure of hybrid hydrogels is also dominated by the POSS content. The degradation rate can be tuned by the POSS content, and a higher POSS content corresponds to a slower degradation rate.

## 1. Introduction

Poly(ethylene glycol) (PEG) hydrogels have been widely used in tissue engineering and drug delivery due to the attractive features of PEG, including superior hydrophilicity, high biocompatibility and lack of immunogenicity [1–3]. The degradability of PEG hydrogels can be conferred by the incorporation of degradable components via hydrolytic, enzymatic or environmental pathways [4–6]. Moreover, the mechanical properties of PEG hydrogels can be regulated by changing the molecular weight and concentration of PEG [7,8], forming “double network” [9,10] and introducing inorganic or inorganic-organic enhanced agents into hydrogels [11,12]. Inorganic-organic composite materials are new generation of high-performance materials combining properties both of inorganic phase and organic phase [13], which have been attracting great attention by the material scientists and chemists.

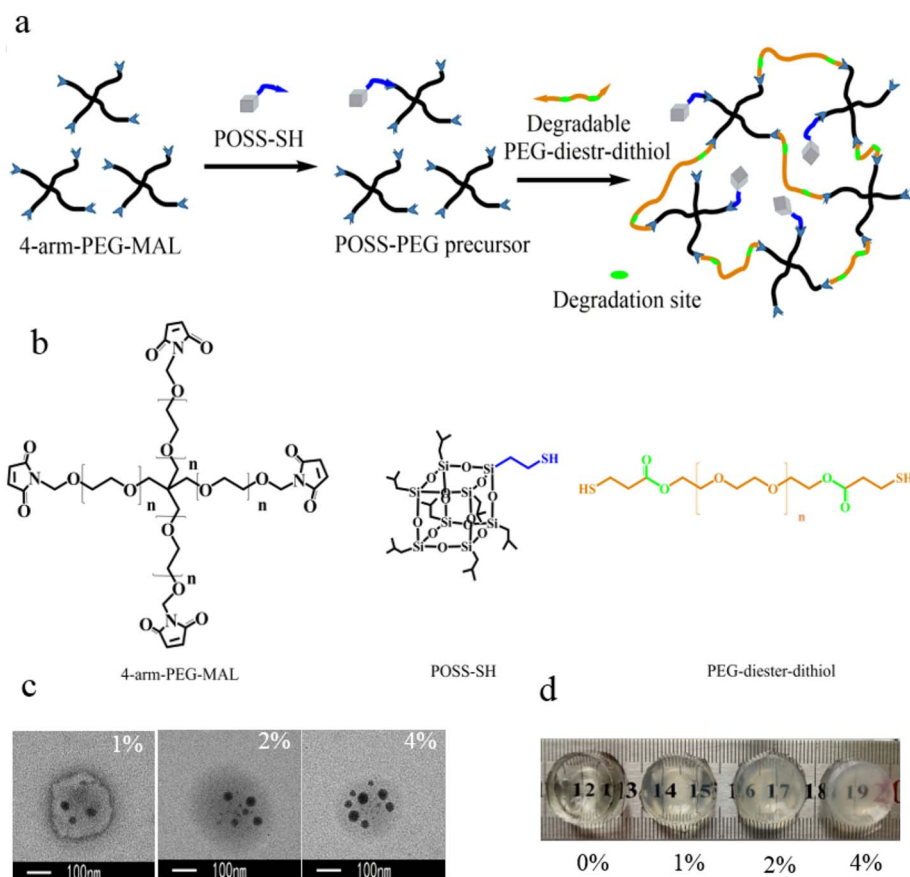
Polyhedral oligomeric silsesquioxanes (POSS) are a family of inorganic-organic hybrid molecules which consist of a cage-like inorganic core and eight variable organic vertex groups [14]. Among all the

hybrid materials, POSS have been attracting great attention for the preparation of inorganic-organic hybrid hydrogels since incorporation of small amounts of POSS can cause significant changes in hydrogels properties due to the special surface properties and high mechanical stability of the nanosize particles [15–17]. A number of POSS-PEG hybrid hydrogels have been prepared by copolymerizing POSS into polymer matrix to enhance their mechanical properties [18–24]. Pan et al. successfully prepared a series of POSS-PEG hybrid hydrogels via a fast azide-alkyne click reaction between octa-azido-functionalized POSS and alkyne-functionalized PEG in DMF [19]. Wang et al. attempted to improve the water solubility of POSS by functionalized it with PEG400, and then incorporated functionalized POSS into a hydrogel network based on triblock copolymers of poly (lactide-*b*-ethylene glycol-*b*-lactide) diacrylates using a redox-initiated polymerization. Regrettably, the gel formation is still proceeded in a 25 wt% acetone-water mixture [20]. Summarily, most of the reported POSS-PEG hydrogels were prepared in organic solvents or mixed solvents since the high hydrophobicity of POSS. So, the current work aims to improve the water

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**Fig. 1.** Preparation of POSS-PEG hybrid hydrogels. a) The scheme for preparation of POSS-PEG hybrid hydrogel. b) The chemical structure of each monomer. c) TEM images of the amphipathic POSS-PEG precursor in water. d) The photographs of different amount of POSS containing hydrogel swollen in deionized water.

solubility of hydrophobic POSS by covalently grafting hydrophobic POSS onto hydrophilic 4-arm-PEG-maleimide to form an amphipathic precursor and further prepare novel POSS-PEG hybrid hydrogels in aqueous phase completely.

Previously, we have prepared maleimide cross-linked PEG hydrogels via Michael-type addition [25]. Compared to free-radical initiated polymerization, Michael-type addition polymerization avoids the use of cytotoxic free-radicals and UV light. Moreover, the maleimide group is widely used because of its fast reaction kinetics and high specificity for thiols at physiological pH. Herein, we prepared a series of hydrolytically degradable POSS-PEG hybrid hydrogels by covalently grafting POSS onto 4-arm-PEG-MAL and further cross-linking with PEG-diester-dithiol by Michael-type addition in aqueous phase, which is free of metal catalyst, UV irradiation and the toxic free-radicals. Moreover, FTIR spectra, morphology structure, mechanical properties, swelling and degradation properties of the resulting hydrogels were investigated.

## 2. Experimental

### 2.1. Materials

4-Arm-PEG-maleimide (4-arm-PEG-MAL,  $M_n = 20$  kDa) was purchased from the Jenkem Technology Co., Ltd. (Beijing, China). 3-Mercaptopropyl isobutyl-POSS (POSS-SH) was supplied by Sigma-Aldrich Co. (USA). Poly (ethylene glycol)-diester-dithiol (PEG-diester-dithiol) was synthesized according to the literature [7]. Solvents such as tetrahydrofuran (THF), concentrated hydrochloric acid (HCl) in analytical grade were purchased from Sinopharm Chemical Reagent Co. (Wuhan, China). All chemicals were used as received without further purification unless otherwise indicated.

### 2.2. Preparation of POSS-PEG hybrid hydrogels

The method for preparation of POSS-PEG hybrid hydrogels is presented in Fig. 1. The various POSS-PEG hybrid hydrogels were prepared by covalently grafting POSS-SH onto 4-arm-PEG-MAL and further cross-linking with PEG-diester-dithiol. Briefly, the mixture of 4-arm-PEG-MAL and different amount of POSS-SH was dissolved in 10 mL THF with stirring at room temperature for 3.5 h. After reaction, THF was removed through rotary evaporation. Then the obtained products and PEG-diester-dithiol (molar ratio of MAL to SH was 1:1) were dissolved in triethanolamine solution (TEA; pH = 7.4, 4 mM) at a specific concentration of 7.5 wt%. The prepolymers were mixed by vortexing before transferred to mold for gelation at 37 °C. The gelation time was determined as the time when the hydrogels would no longer flow by the force of gravity [26,27].

### 2.3. Transmission electron microscopy (TEM)

TEM images were taken with Tecnai G20 (FEI American). POSS-PEG precursor solution was prepared in water at a concentration of 3 mg/mL. An aliquot of the sample solution was cast onto a copper grid and sample was left to dry on the grid before TEM examination.

### 2.4. FTIR spectra

All hybrid hydrogels were swelled in deionized water and dehydrated by freeze-dried in a Freeze Drier (Beijing boyikang Lab Instrument Co., Ltd.) under vacuum at  $-50$  °C for at least 48 h until all the solvent was sublimed. The FTIR spectra were collected on dried hydrogels at a resolution of  $2\text{ cm}^{-1}$  in the range of  $4000$  to  $600\text{ cm}^{-1}$  for a total of 16 scans using a Nicolet IS 50 spectrometer (ThermoFisher Scientific Co.) equipped with an ATR sampling unit (25 °C).

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