

Original article

A hybrid hydrogel based on clay nanoplatelets and host–guest inclusion complexes

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ARTICLE INFO

Article history:

Received 28 December 2015

Received in revised form 1 February 2016

Accepted 23 February 2016

Available online 2 March 2016

Keywords:

Host–guest chemistry

Clay

Supramolecular hydrogel

Cyclodextrin

Electrostatic interaction

ABSTRACT

In this work, a monomer with double bond was introduced to the surface of clay nanosheets *via* inclusion complexation between cyclodextrin (CD) host and azobenzene (Azo) guest, as well as electrostatic interaction between clay nanoplatelets and cations of azobenzene derivatives. The obtained supra-structure acts as a supramolecular cross-linker in its copolymerization with macromonomer PEG resulting in a hybrid supramolecular hydrogel. Only viscous liquid was obtained in the absence of clay nanoplatelets, revealing the supramolecular cross-linker played an important role in the hydrogel formation. Such hybrid supramolecular hydrogel exhibited good stability and shear thinning property. © 2016 Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences.

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1. Introduction

Supramolecular hydrogels have attracted increasing attention due to their promising applications in biotechnology and bioengineering, which originated from their unique characters, such as self-healing property based on their reversibility, rich chemical functionality and well-defined nanostructures [1–4]. Compared with the conventional hydrogels connected through covalent interactions, supramolecular hydrogels are formed *via* non-covalent interactions, including hydrogen bond, π – π stacking, electrostatic interaction, metal–ligand interaction, hydrophobic interaction as well as host–guest inclusion complexation *etc.* [5–9]. Owing to the inherent reversible properties of the non-covalent interactions, supramolecular hydrogels are featured by stimuli-response and thixotropy *etc.* [10–12].

In recent years, supramolecular hydrogels based on the complexation between cyclodextrins (CD) and guest molecules have gained much attention because of their potential applications in the field of biomedical engineering [13–15]. As pioneers in this field, Harada and his co-workers obtained macroscopic supramolecular hydrogels using poly(acrylamide) functionalized with host (cyclodextrin) or guest (adamantane, ferrocene, or azobenzene)

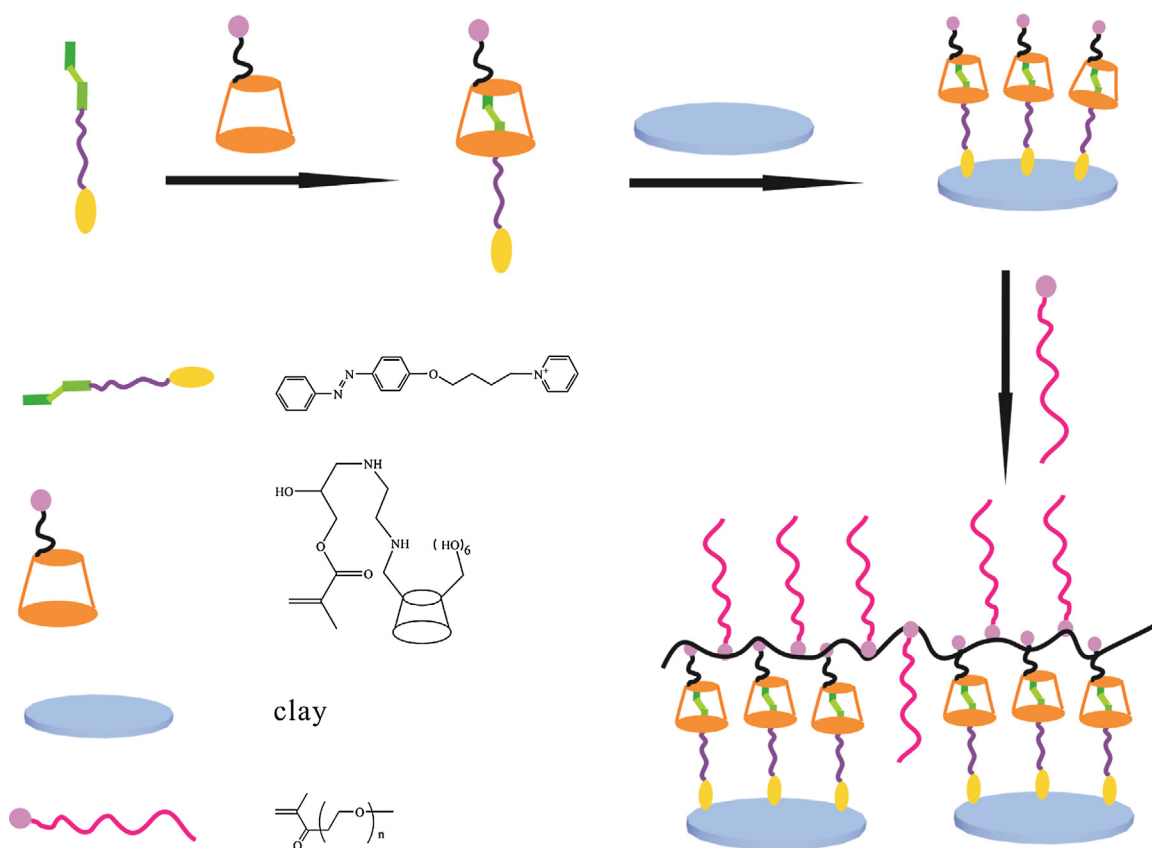
moieties [16,17]. These hydrogels exhibited self-healing properties and the strength of such supramolecular materials could be restored completely through host–guest interactions. However, the synthesis process of these host or guest functionalized polymers is always time-consuming and expensive. In particular, a drawback of the conventional polymeric hydrogels (OR gels) is mechanically weak and brittle property [18].

To enhance the strength of OR gels, clay was utilized and demonstrated to be effective [19,20]. Generally, clay was introduced into the hybrid hydrogels by intercalating cationic surfactants into clay sheets in order to expand the spaces between clay sheets, followed by adding monomers, which were further polymerized to produce hydrogels [19]. In this method, cationic surfactants play the role of intercalative agents, which are indispensable to improve the compatibility of clay with organic compounds. Moreover, the addition of intercalative agents makes the hydrogels complicated. In the past few years, Prof. Haraguchi had prepared nanocomposite hydrogels (NC gels) with high mechanical properties, which were composed of specific polymers and a water-swallowable inorganic clay [18,20–22]. However, specific polymers were utilized in this system, which may limit its application.

To incorporate inorganic species to supramolecular hydrogels, Jiang's group proposed a concept of "supramolecular cross-linker" (SCL) [1]. Based on this strategy, SiO₂, quantum dots (QDs) and graphene have been successfully introduced into the hybrid hydrogels, which exhibited diverse stimuli-response to chemical,

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Scheme 1. Preparation of a hybrid hydrogel based on the supramolecular cross-linker.

redox and thermo changes [1,23–25]. Herein, hybrid hydrogels incorporated clay nanosheets were constructed by the SCL technique (Scheme 1). An azobenzene derivative with a pyridinium cation (Azo-N⁺) and glycidyl methacrylate modified β -CD (GMA-CD) was firstly synthesized. The complex of GMA-CD with Azo-N⁺ was anchored onto the clay surface to form a supra-structure bearing a double bond due to the electrostatic interaction between clay and the pyridinium cation of Azo-N⁺. Finally, the obtained supra-structure acts as a supramolecular cross-linker in its copolymerization with macro-monomer containing PEG leading to a hybrid supramolecular hydrogel, which exhibited good stability and shear thinning properties.

2. Experimental

Materials: β -Cyclodextrin (β -CD) was recrystallized three times from water. *p*-Toluenesulfonyl chloride (TsCl) was recrystallized twice from petroleum ether/acetone mixture. Synthetic hectorite “Laponite XLG” (Rockwood Ltd.: [Mg_{5.34}Li_{0.66}-Si₈O₂₀(OH)₄]Na_{0.66}, layer size = 20–30 nm Φ \times 1 nm, cation exchange capacity, CEC = 104 mequiv 100 g⁻¹), 4-phenylazophenol (Aldrich), *N,N,N',N'*-tetramethylethylenediamine (TEMED, Aldrich) and glycidyl methacrylate (GMA, Acros) and other reagents were commercially available and used as received.

Characterization techniques: ¹H NMR spectra were recorded on a Bruker DMX500. UV–vis spectra were taken on a Perkin-Elmer Lambda 35 UV–vis spectrophotometer. FT-IR spectra were recorded on a Nexus 470 FT-IR spectrometer on powder-pressed KBr pellets. Thermal gravimetric analysis (TGA) measurements were carried out on a Perkin Elmer Pyris-1 series thermal analysis system under a flowing nitrogen atmosphere at a scan rate of 20 °C min⁻¹ from 50 °C to 700 °C. The rheological behavior of the

hydrogels was investigated by a Malvern rheometer using a 40 mm parallel-plate geometry, cone-plate geometry or cup-bob at 25 °C. Oscillating strain was fixed at 0.1% for all dynamic tests. ITC was carried out on MicroCal VP-ITC at 25 °C.

Synthesis of 1-(4-(4-(phenyldiazenyl)phenoxy)butyl)pyridinium bromide (Azo-N⁺): The synthetic route of Azo-N⁺ was illustrated in Scheme 2.

Synthesis of 1-(4-(4-(bromobutoxy)phenyl)-2-phenyldiazeno)pyridinium bromide (Azo-Br): To an acetone solution of 4-(phenyldiazenyl)phenol (5 g, 25 mmol) and 1,4-dibromobutane (6 mL, 50 mmol), K₂CO₃ (7.65 g, 55 mmol) were added. The reaction mixture was allowed to reflux for 24 h under an atmosphere of nitrogen. After cooling to room temperature, the mixture was filtered, concentrated, and recrystallized in petroleum ether, followed by purification by silica gel column chromatography.

Synthesis of 1-(4-(4-(phenyldiazenyl)phenoxy)butyl)pyridinium bromide (Azo-N⁺): A solution of Azo-Br (2 g, 6 mmol) in 30 mL DMF and pyridine (2.5 mL, 30 mmol) was allowed to react at 100 °C for 24 h. After being cooled to room temperature, the mixture was concentrated and precipitated from petroleum ether, followed by recrystallization from ethanol. The ¹H NMR spectrum of Azo-N⁺ in DMSO (Fig. S1 in Supporting information) demonstrated the successful synthesis.

Synthesis of glycidyl methacrylate modified β -CD (GMA-CD): GMA-CD was synthesized according to the literature [26].

Preparation of the hybrid hydrogel: A certain amount of clay was added to an aqueous solution of Azo-N⁺ (0.08 g) and GMA-CD (0.4 g), followed by stirring for 24 h. Then K₂S₂O₈, *N,N,N',N'*-tetramethylethylenediamine (TEMED) and poly(ethylene glycol) (PEG) macro-monomer were added. The mixture was allowed to react for 6 h under an atmosphere of nitrogen and the hybrid hydrogel was obtained.

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