



# Nanocomposite hydrogel incorporated with polymerizable liquid crystal surfactant: Shape transition from layered to honeycomb pore structure and thermo/swelling behavior



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## ABSTRACT

In order to investigate the relationship between nanocomposite hydrogels and polymerizable liquid crystal surfactant, under the physical cross-linking of nanoclay lithium magnesium silicate hydrate (LMSH), a series of poly(NIPAm-LMSH-AAC-Brij-58) nanocomposite hydrogels, based on the copolymerization of polymerizable liquid crystal AAC-Brij-58 synthesized by esterification reaction and *N*-isopropylacrylamide (NIPAm), were synthesized by in situ free-radical polymerization. The results show that with increasing AAC-Brij-58 concentration from 0 to 1 wt%, the particle sizes decrease from approximately 143 to 60 nm, and the appearance becomes cruciform or flower type and rod shape, respectively. The obtained nanocomposite hydrogels present thin pore walls and larger pore diameters. With increasing mass ratios of AAC-Brij-58/NIPAm from 0 to 1/15, the maximum swelling ratios exhibit an increasing tendency, the volume phase transition temperatures increase from 32.10 to 33.56 °C, and thermal degradation temperature increase from 305 to 340 °C.

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## 1. Introduction

Nanocomposite hydrogels are a type of new intelligent nanocomposites obtained by polymerization of inorganic nanoclay and functional monomer. Recent advances in chemical, physical, and biological fields together with increasing demands in biomedical and pharmaceutical sectors have led to new developments in nanocomposite hydrogels for many diverse applications [1–3]. For nearly the past two decades, intelligent polymeric nanocomposite hydrogels that are sensitive to external stimuli (e.g., temperature [4–6], salt concentration [7], magnetic effect [8], mechanical stress [9], light [10], pH [6], and electric fields) have attracted much scientific interest as water absorbents, sensors, and lubricants. Nanocomposite hydrogels not only exhibit unique soft/wet properties and biocompatibility [11], but also show high mechanical strength, appreciable transparency, and high sensitivity to temperature and magnetic and electric fields. On the contrary, the traditional organic hydrogels cross-linked by chemical cross-linkers such as *N,N'*-methylenebisacrylamide (MBA) display several major drawbacks such as opacity under high cross-linker concentrations, narrow pore

size, lower equilibrium swelling ratio (ESR), and slow deswelling [12–14].

Since the use of inorganic nanoclay hectorite as a physical cross-linking agent to prepare poly(*N*-isopropylacrylamide) (PNIPAm)/hectorite nanocomposite hydrogels by in situ free-radical polymerization was first reported by Haraguchi et al. [15], nanocomposite hydrogels with enhanced mechanical properties and quick response have attracted much research interest. Meanwhile, Stempfle et al. [16] investigated the diffusion of Laponite clay nanoparticles, and found anomalous diffusion of the clay nanoparticles demonstrating viscoelastic behavior because of their function as cross-linkers of PNIPAm chains. The mobility changes significantly around the volume phase transition temperature (VPTT) of the PNIPAm hydrogel. Afterward, Liao et al. [17] reported a facile solution-polymerized approach to prepare nanocomposite hydrogels by electrostatic assembly of positive TiO<sub>2</sub> nanoparticles with negative clay nanosheets, finding that TiO<sub>2</sub>-clay composite particles exhibit high transparency and the maximum compressive strength (598.21 kPa). Recently, Ye et al. [18] have presented a photopolymerization approach to prepare a polymer/clay nanocomposite gel with electrorheological response, whose mechanical strength under electrical field could be enhanced by the noncovalent effect. Since 2002, the conception of nanocomposite hydrogel has been accepted by all researchers. However, because of the unique physical cross-linking, the

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combination between nanocomposite hydrogels and liquid crystal is still unknown despite the description of liquid crystal-based hydrogels by Gong et al. in 2000 [19].

On the contrary, as an important component of liquid crystal-based hydrogels, the liquid crystal-templated hydrogels have been widely studied owing to their advantages in producing uniform porous structure in the hydrogel network and improving responsiveness and mechanical properties of the hydrogels. For example, by using surfactant as a lyotropic liquid crystal template, a threefold increase in both compressive modulus and diffusive transport was observed and surface areas  $>700 \text{ m}^2/\text{g}$  and nanostructured hydrogel hydrocarbon sorption capacities of  $0.7 \text{ cm}^3/\text{g}$  were obtained by Clapper et al. [20] and Beck et al. [21]. Monteiro et al. [22] prepared well-functioning liquid crystal-based hydrogels using lauryl sodium sulfate and dodecyl fatty alcohol as the template. In our previous study, using nonionic surfactant polyoxyethylene-20-cetyl ether (Brij-58) as template, hydrogel-based chemical cross-linking agent, MBA, and physical cross-linking agent, inorganic nanoclay lithium magnesium silicate hydrate (LMSH), were prepared [23–25]. It was found that the introduction of Brij-58 caused the formation of numerous pores and thin pore wall, leading to rapid swelling or deswelling ratio and enhanced mechanical properties [26, 27]. However, in the aforementioned hydrogel system, amphiphilic Brij-58 acts only as a pore-forming agent and can be washed out after removal. In other words, the character of liquid crystal monomer Brij-58 cannot influence the hydrogel network. In order to avoid template function of Brij-58 molecules and retain the property of liquid crystal, Brij-58 was modified by esterification reaction with acrylic acid (AAc) to obtain polymerizable AAc-Brij-58. On the basis of this consideration, traditional poly(NIPAm-MBA-AAc-Brij-58) hydrogels, which present significant bovine serum albumin (BSA) adsorption, were synthesized. However, the chemical structure, pore shape, and properties of nanocomposite hydrogels are completely different from those of MBA cross-linked hydrogel, because of the diversity in cross-linking mechanism.

In this study, in order to compare the difference and investigate the relationship between nanocomposite hydrogels and liquid crystal molecules, a series of liquid crystal-based nanocomposite hydrogels, poly(NIPAm-LMSH-AAc-Brij-58), were synthesized by free-radical polymerization under the cross-linking action of inorganic nanoclay LMSH and synthesis of polymerizable liquid crystal monomer AAc-Brij-58 by esterification reaction. The particle size and shape of AAc-Brij-58 in distilled water were determined by multiple light scattering (MLS), dynamic light scattering (DLS), and transmission electron microscopy (TEM). The chemical composition and crystal structure of the obtained nanocomposite hydrogels with various mass ratios of AAc-Brij-58/NIPAm were confirmed by Fourier transform infrared (FTIR) spectroscopy (FTIR), nuclear magnetic resonance ( $^1\text{H}$  NMR), and X-ray diffraction (XRD). The interior pore morphology was observed by scanning electron microscopy (SEM). Temperature sensitivity, thermostability, and swelling dynamics were investigated by differential scanning calorimeter (DSC), thermogravimetric analysis (TGA), and weighing method.

## 2. Experiments

### 2.1. Materials

*N*-isopropylacrylamide (NIPAm, 95%, Tokyo Kasei Kogyo Co. Ltd) was purified by recrystallization from a toluene/*n*-hexane mixture. The nonionic surfactant polyoxyethylene-20-cetyl ether (Brij-58,  $M_w = 1123.5$ , Germany SERVA Company) was used as received. AAc-Brij-58 was prepared in our laboratory according to the method proposed by Liu et al. [28] Inorganic nanoclay LMSH was purchased from Luancheng Zixin Industrial and Trading Co., Ltd (China). Initiator ammonium persulfate (APS) and accelerator *N,N,N',N'*-tetramethylethylenediamine (TEMED) were purchased from Beifang

Tianyi Chemical Reagent and China East Normal University Chemical Factory, Shanghai, respectively. Water used in the whole experiment was of Millipore Milli-Q grade.

### 2.2. Synthesis of poly(NIPAm-LMSH-AAc-Brij-58) nanocomposite hydrogels

In brief, AAc-Brij-58 with various contents was first dissolved in 10 mL of distilled water until a transparent solution was obtained. Monomer NIPAm was subsequently added to this solution at  $25^\circ\text{C}$  under constant stirring and  $\text{N}_2$  atmosphere for 30 min. Then, 1.77-wt% LMSH was added under constant stirring. Thereafter, 0.13-wt% APS and 0.55-wt% TEMED were added. After 5 min, the resulting solution was poured into a 2.0-mm-thick glass mold, and sealed before placing it in the thermostat and polymerization for 48 h at  $25^\circ\text{C}$ .

The resulting poly(NIPAm-LMSH-AAc-Brij-58) hydrogels were simply labeled as APHX. In this study, the mass ratio of AAc-Brij-58/NIPAm is expressed as X. For example, the nanocomposite hydrogel synthesized by 0.01-g AAc-Brij-58/1.5-g NIPAm/0.2-g LMSH is expressed as APH01. Finally, the resultant hydrogels were taken out from the glass molds and cut into disks of 1-cm diameter with punch, and immersed in an excess of water for 48 h to remove impurities by changing water several times.

### 2.3. Characterization

#### 2.3.1. Multiple light scattering

In order to investigate stability of size and concentration of AAc-Brij-58 particles in aqueous solutions under transmitted light and backscattered light, MLS (Turbiscan Lab, France) was used with near-infrared light as light source. The samples were placed in a 20-mL measuring cell to test 24 times at  $25^\circ\text{C}$  once an hour.

#### 2.3.2. Dynamic light scattering

In order to analyze the particle size and distribution of AAc-Brij-58 in aqueous solution, samples in solution with concentration varying from 0.1 to 1 wt% were tested thrice using a Malvern laser particle size analyzer (ZS90, England) through DLS instrument.

#### 2.3.3. Transmission electron microscopy

In order to compare the shape of the Brij-58 and AAc-Brij-58, the sample solutions were first casted on a carbon-coated copper grid and dried at  $25^\circ\text{C}$ . The morphologies of the APH nanocomposite hydrogel samples were observed on an H-7650 transmission electron microscope (Hitachi Inc., Japan).

#### 2.3.4. X-ray diffraction

XRD curves of freeze-dried APH nanocomposite hydrogel samples were achieved on a Bruker D8 Advance X-ray diffractometer (Germany) with  $\text{Cu}/\text{K}\alpha$  radiation at a wavelength ( $\lambda$ ) of  $1.5406 \text{ \AA}$ , scan speed of  $2^\circ/\text{min}$ , step size of  $0.02^\circ$ , and  $2\theta$  scan range of  $2.0\text{--}80^\circ$ .

#### 2.3.5. Scanning electron microscopy

In order to retain the original pore structure, the swollen APH nanocomposite hydrogel disks were freeze-dried at  $-50^\circ\text{C}$  for 12 h on an FD-1A-50 freeze-drier to remove any water present. After the cross sections of specimens were fractured carefully, the interior morphologies were observed on a Quanta 200 scanning electron microscope (FEI Company) at 20 kV after sputter-coated with gold under vacuum.

#### 2.3.6. Swelling and deswelling kinetics

Swelling behaviors of the APH nanocomposite hydrogels were obtained by immersing the specimens into excess of deionized water at  $25^\circ\text{C}$  by changing the water several times. The maximum

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