



# Hydrophobic association mediated physical hydrogels with high strength and healing ability

Yuhui Geng<sup>b</sup>, Xiao Ying Lin<sup>a</sup>, Pengju Pan<sup>b, \*\*</sup>, Guorong Shan<sup>b</sup>, Yongzhong Bao<sup>b</sup>,  
Yihu Song<sup>a</sup>, Zi Liang Wu<sup>a, \*</sup>, Qiang Zheng<sup>a</sup>

<sup>a</sup> MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, 310027, China

<sup>b</sup> State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou, 310027, China

## ARTICLE INFO

### Article history:

Received 29 May 2016

Received in revised form

16 July 2016

Accepted 6 August 2016

Available online 8 August 2016

### Keywords:

Hydrogels

Hydrophobic association

Stimuli-triggered healing

Shape memory

## ABSTRACT

Supramolecular polymeric hydrogels, combining the responsiveness of noncovalent interactions and good mechanical properties of polymers, have received increasing attentions due to their high strength, multi-responses to stimuli, and good processability. In this article, we develop transparent physical hydrogels by simply casting and reswelling the films of copolymers synthesized by polymerization of a hydrophilic monomer of acrylic acid (AA) with a small fraction of hydrophobic monomer of stearyl acrylate (SA). The long alkyl chains of SA units segregate in water to form hydrophobic associations, serving as the physical crosslinking junctions of gels. The gels are robust with tensile strength up to ~2 MPa; the mechanical properties can be tuned by varying the composition of copolymers and depend on the deformation rate. The gels are responsive to temperature, pH, and ethanol solvent, which mediate the stability of the hydrophobic associations and even lead to gel-to-sol transition. Based on this reversible transition, the gels show stimuli-mediated healing ability. Gels with complex structures can be constructed by localized welding. In addition, the gels exhibit shape memory behaviour; the shape can be memorized by forming strong coordination between carboxylic acid groups and additional Fe<sup>3+</sup> ions and relaxed by reduction of the Fe<sup>3+</sup> ions. These gels with versatile properties should find applications such as in responsive coatings, tissue engineering, and soft actuators.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

The last three decades have witnessed the fast developments of hydrogels, which have similarity to soft tissues, versatile responses to external stimuli, and broad applications in tissue engineering, drug delivery, soft actuators, etc [1–3]. The innovation of novel hydrogels with advanced properties or functions has greatly facilitated these developments. For example, Gong et al. have developed the double network principle to toughen hydrogels with excellent mechanical strength [4–6]; the resultant gels can be used as load-bearing artificial organs and actuators [6–9]. Aida and co-workers have fabricated anisotropic hybrid hydrogels with cofacially aligned nanosheets, which show direction-dependent optical

and mechanical properties, as well as extraordinary fast and reversible contraction without water uptake and release; these gels are ideal candidate to build optical devices and soft actuators [10,11].

To meet special requirements, it is desired to develop hydrogels with multiple functions and high performances. For example, three-dimensional (3D) printed hydrogels are promising in artificial organs with complex structure and scaffolds for cell culture; it needs the gel material to be robust yet printable, which means that the precursor solution can be readily gelled or has a fast sol-to-gel transition [12,13]. High strength physical hydrogels with tunable sol-to-gel transition should be an ideal candidate; however, most physical hydrogels such as jelly and collagen gels are weak. To develop robust physical gels with controllable sol-to-gel transition, supramolecular chemistry should be an effective approach. Supramolecular polymer gels are viscoelastic materials assembled by intermolecular noncovalent interactions [14,15]. If the strength of multiple noncovalent bonds on a polymer chain is comparable to

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [wuziliang@zju.edu.cn](mailto:wuziliang@zju.edu.cn) (Z.L. Wu), [panpengju@zju.edu.cn](mailto:panpengju@zju.edu.cn) (P. Pan).

that of covalent bonds, the physical hydrogels will be of high strength. In recent years, tough physical hydrogels have been developed via the formation of polyion complex, multiple hydrogen bonding, and metal coordination, which possess high strength up to megapascal, self-healing, or shape memory properties [16–20].

Hydrophobic interaction is widely used in molecular self-assembly of block copolymers to form supramolecular gels, which are usually responsive yet mechanically weak [21–23]. To form tough supramolecular polymer hydrogels, the polymers should contain balanced hydrophilic groups to maintain water and hydrophobic groups to strongly associate as crosslinked junctions. Physical hydrogels mediated by hydrophobic association have been developed by compression moulding the copolymers and subsequently swelling the films in water [24–27]. In addition, tough and self-healable hydrogels are developed by copolymerizing hydrophilic and hydrophobic monomers in a micellar solution of sodium dodecyl sulfate [28–34]. These physical gels show breaking stress and strain in tension of 0.2–0.5 MPa and 1000–2000%, respectively.

In this paper, we reinvent the classic system of acrylic acid (AA) and stearyl acrylate (SA) found by Osada and his coworkers. They prepared a chemically crosslinked hydrogel with shape memory properties by copolymerizing the two monomers with molar fraction of SA larger than 0.25, in the presence of *N,N'*-methylenebisacrylamide as the crosslinker. The alkyl chains of SA units form crystalline domains to freeze the temporary shape, which can recover to the original shape by melting the crystalline domains at high temperature [35–39]. At room temperature these hydrogels are whitish and fragile. In addition, gel-to-sol transition is absent due to the existence of chemically crosslinked network.

We report here robust physical hydrogels developed by casting the poly(SA-co-AA) ethanol solutions and swelling the resulting films in water. The fraction of SA is decreased to several percentages, so that transparent hydrogels with high tensile strength are obtained. The long alkyl chains of SA units form hydrophobic domains with different extent of crystallization, acting as the physical crosslinking junctions of the copolymers. The water content and mechanical property can be tuned by varying the composition of copolymers. These gels are responsive to temperature, pH, and ethanol solvent, which tune the stability of hydrophobic associations and lead to a gel-to-sol transition and healing ability. The microstructures and gel-to-sol transition mechanism of these physical gels are investigated by wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS). These physical gels with high strength and healing ability are facile to fabricate and reconstructable, which should find applications as membranes, coatings, cell scaffolds, etc.

## 2. Experimental section

### 2.1. Materials

Acrylic acid (AA, Sinopharm Chemical Reagent Co., Ltd.) was purified by vacuum distillation at 90 °C before use. Stearyl acrylate (SA, Tokyo Chemical Industry Development Co., Ltd.) and 2,2'-azobis(isobutyronitrile) (AIBN, Sigma-Aldrich) were recrystallized from ethanol. Ethanol was distilled before use. Deuterated dimethyl sulfoxide (DMSO-*d*<sub>6</sub>, J&K Scientific Ltd.) for NMR measurements was used as received. Water was purified by ultra-pure water system (Heal Force).

### 2.2. Synthesis of poly(SA-co-AA)

Poly(SA-co-AA) with various composition, *F* (defined as the

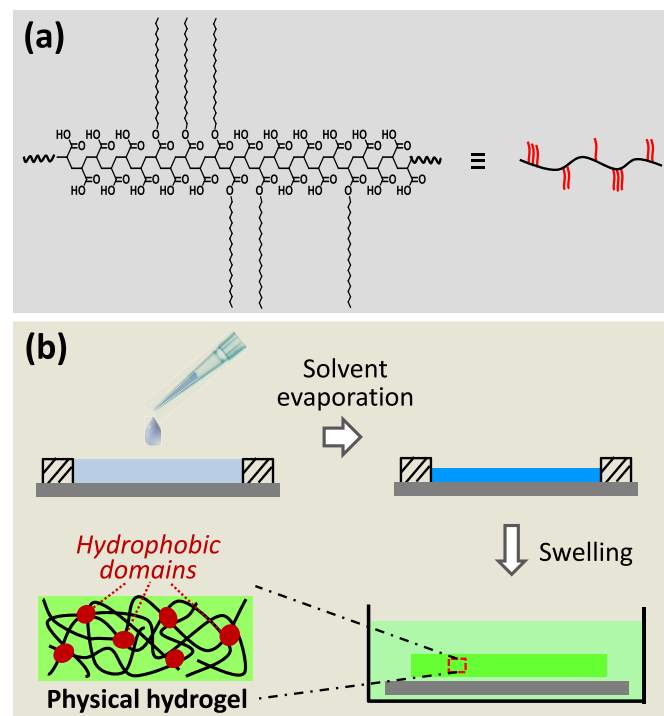
molar fraction of SA in the total monomers), was synthesized by free radical copolymerization of AA and SA in ethanol. The process is similar to the synthesis of chemical gels reported by Osada et al., except the absence of chemical crosslinker [35–39]. A representative process is described here to synthesize poly(SA-co-AA) with *F* = 0.15. 11.14 g (154.6 mmol) of AA, 8.86 g (27.3 mmol) of SA, and 0.20 g (1 wt%, relative to the total mass of monomers) of AIBN were added into 50 mL ethanol to form a homogeneous solution in a Schlenk flask. After degassing the solution with argon for 30 min at room temperature, the polymerization was carried out at 60 °C for 10 h under an argon atmosphere. The obtained product, a viscous solution, was precipitated in ether; the precipitate was dried *in vacuo* at 50 °C for 3 days to yield transparent dry solid of poly(SA-co-AA). Other copolymers with different *F* were synthesized by a similar process (Table S1).

### 2.3. Preparation of the gel film

The copolymers were dissolved in ethanol to form homogeneous solutions with polymer concentration of 0.14 g/mL. Then, the poly(SA-co-AA) solution was dripped onto a horizontally placed glass plate with silicone rubber fixed at the edge. After the solvent gradually evaporated at room temperature, the sample was immersed in a large amount of water to obtain swollen hydrogel (Fig. 1). The film was peeled from the glass substrate after several hours; however, the swelling process was continued for several days to achieve equilibrium. Thus obtained hydrogels are coded as SA-*F*, in which *F* is the molar fraction of SA in feed.

### 2.4. Characterization

The composition of copolymers was characterized by <sup>1</sup>H NMR (400 MHz Bruker AVANCE II NMR spectrometer, Bruker BioSpin Co.,



**Fig. 1.** (a) Molecular structure of poly(SA-co-AA). (b) Schematic for the preparation of physical gel by casting ethanol solution of the copolymer and swelling the sample in water to obtain the swollen gel with segregated hydrophobic associations as the physical crosslinking junctions.

Download English Version:

<https://daneshyari.com/en/article/5178939>

Download Persian Version:

<https://daneshyari.com/article/5178939>

[Daneshyari.com](https://daneshyari.com)