

# Robust bonding and one-step facile synthesis of tough hydrogels with desirable shape by virtue of the double network structure†

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Robust bonding of a hydrogel in aqueous environment, either to another hydrogel or to a solid, is one of the major unsolved issues for the practical applications of hydrogels in various fields. Here we report robust bonding between a pair of hydrogel sheets, containing over 90 wt% of water, by applying the double-network (DN) structure. In the optimal condition, the peeling energy of the united gel sheets reaches 1200 J m<sup>-2</sup>, which is comparable to the bulk fracture energy of a normal type of tough DN gels. This hydrogel bonding technique is also applied to form tough bonding between hydrogel and plastic plates. Furthermore, based on this technique, we have developed a facile method to synthesize robust double network hydrogels with any desirable free-shape from micro-gel precursors. These novel techniques will substantially merit the applications of the tough hydrogels in various fields, such as an artificial meniscus.

## Introduction

Polymer hydrogels had been too brittle and too weak to be used as any load-bearing materials until the beginning of 2000. Since 2001, several different approaches to improve extraordinarily the mechanical strength of hydrogels had been proposed.<sup>1-7</sup> Our group have developed novel high-strength and high toughness hydrogels<sup>3</sup> by introducing a strongly asymmetric double network (DN) structure inside the hydrogels, which were composed of a tightly cross-linked polyelectrolyte gel that is highly swollen in water as the first network, and a sparsely cross-linked neutral polymer that is densely packed in the polyelectrolyte gel as the second network. This kind of asymmetric structure is obtained *via* a two-step sequential free-radical polymerization process of the two networks. The DN gels synthesized under an optimal condition, despite of over 90 wt% water content, exhibit extraordinary mechanical performances in terms of its high Young's modulus (~0.3 MPa), fracture stress (~20 MPa), and fracture energy (~1000 J m<sup>-2</sup>),<sup>3,8-11</sup> which correspond to the performances of the human articular cartilage. The inventions of these hydrogels with high mechanical performance substantially

broaden their potential application in various fields, for example, as substitute of articular cartilage,<sup>12</sup> scratchproof coating materials,<sup>13</sup> cell-sheet cultivation,<sup>14</sup> antifouling materials,<sup>15</sup> *etc.*

In the practical applications of hydrogel systems, some problems still remain: (1) weak bonding of a hydrogel in aqueous environment, either to another hydrogel or to a solid by using conventional glues due to the high water content of gels; (2) low freedom to form various desirable shapes. For example, due to the two-step sequential polymerization process of a DN gel, it is not possible to synthesize a tough DN gel with a complicated shape, such as the shape of a meniscus in human joint; (3) poor processability, especially for the DN gels. The first polyelectrolyte network that is highly swollen in water is usually too brittle and weak to handle. Furthermore, the two-step polymerization process in the preparation of the DN gels is very time consuming since the monomer diffusion of the second component is involved in the preparation. These problems hinder the practical application and large-scale production of DN gels. Here we report a breakthrough, which solves these problems simultaneously. The breakthrough starts from the invention of the strong bonding between swollen hydrogels, taking advantage of toughening mechanism of the DN gels. Based on this invention of bonding, we further develop a simple technique to prepare high-strength DN gels from particle gel precursors. These achievements, with no doubt, will substantially promote the industrial based large-scale production and various applications of high-strength gels, such as medical transplantation, tissue engineering, and lab-on-a-chip technology.

## Experimental

### Preparation of normal DN gels and bonded DN gels

2-Acrylamido-2-methylpropanesulfonic acid (AMPS or ATBS) was a courtesy from Toagosei Co., Ltd. and used as received. Acrylamide (AAm) (Junsei Chemical Co. Ltd) was recrystallized from chloroform. *N,N'*-Methylenebis (acrylamide) (MBAA;

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† Note: it should be noted that in our previous papers,<sup>8,9,25,26</sup> *G* was calculated by using a different expression, which is not proper according to the definition.