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Design and function of smart polymer gels based on ion recognition

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ABSTRACT

Stimuli-responsive polymer gels can drastically change their volume in response to various external physical and chemical stimuli. The smart polymer gels for specific chemical substances have been extensively studied as applications for molecular recognition or supramolecular chemistry in the material sciences toward intelligent materials. This review article highlights recent advances in the molecular design of stimuli-responsive polymer gels triggered by molecular recognition, especially by the recognition of ionic species.

1. Introduction

Stimuli-responsive polymer gels can drastically change their volume in response to various external physical and chemical stimuli including pH [1–3], temperature [4–6], solvent composition [4,5,7,8], electrical and magnetic fields [9–11], UV/vis light [12–14], and chemicals [15–19]. They have been of much interest due to various applications such as shape-memory materials [20–22], actuators [23,24], artificial muscles [25], and microfluidic devices [26–28]. Among them, the smart polymer gels for specific chemical substances have been extensively studied as applications for molecular recognition or supramolecular chemistry in the material sciences toward intelligent materials. In this short review, we focus on the recent molecular design of ion-responsive polymer gels based on ion receptors and the polymer networks and the change in the swelling properties induced by the ions as stimuli.

The most characteristic property of polymer gels as functional materials is swelling, i.e., the drastic increase in their 3D network in volume or length due to the absorption of solvent molecules. The swelling properties of the polymer gels are generally evaluated by the ratios before and after soaking in them and should be mainly governed by the interaction of the polymer chains in the media and rubber elasticity due to cross-linking of the polymer chains. The good compatibility of the polymer chains with the media expands the network while a poor one collapses it. Densely cross-linked polymer gels should be tough and their swelling abilities should be low, while sparsely cross-linked ones should be soft and high, respectively. In addition to these two factors, in the case of ion-responsive polymer gels that consist of a polymer chain compatible with media and with ion-recognition sites, the osmotic pressure and electrostatic repulsion generated by the complexation significantly expands their network, and association of the ions or the polymer chains as a physical crosslinking collapses them as shown in Fig. 1. Among these effects for the polymer gels, ion recognition so far should be visualized by changes in the volumes, indicating that the supramolecular design is related to the material design.

2. Ion responsive polymer gels

2.1. Metal cations as stimuli

For metal cations, macrocyclic compounds, such as crown ethers and calixarenes, have been attracting considerable interest as molecular receptors, and the polymers containing macrocyclic compounds have been extensively prepared and investigated as separation and extraction material applications for specific metal ions. Such complexations of the polymers with metal ions have led to the design of responsive polymer gels that exhibit large volume changes induced by the metal ions. As a classical example, a stimuli-responsive polymer membrane based on the complexation of crown ether groups with specific metal ions and thermo-sensitivity based on the phase transition of poly(*N*-isopropylacrylamide) (PNIPAM) had been reported by Yamaguchi et al. for the development of ion-gating membranes [29]. More recently, Chu and co-workers reported stimuli-responsive smart microspheres that simultaneously exhibited an ion-recognition property by a similar response of PNIPAM [30,31]. In K^+ solutions, the LCST of the microsphere shifted to a higher temperature and the colloidal stability was increased due to the formation of crown ether/K^+ complexes. The microspheres isothermally underwent a volume

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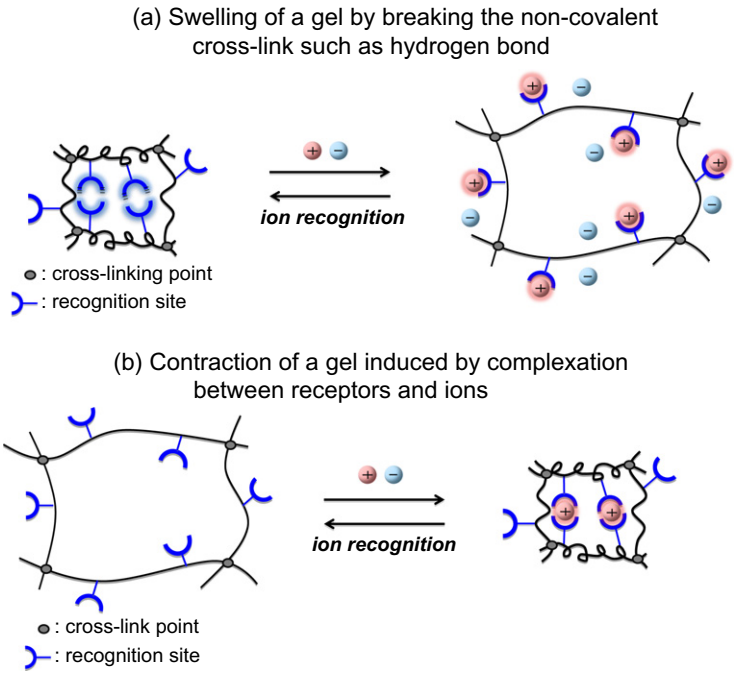

Fig. 1. Some conceptual scheme for stimuli-responsive polymer gels triggered by ions in this review.

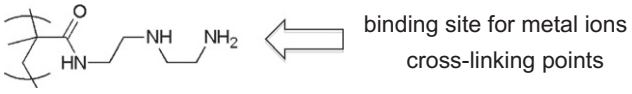

Fig. 2. Structural elements in chemomechanical polymers based on poly(methyl methacrylate) with ethylenediamine groups as binding sites for metal ions, and cross-linking points.

change at a certain temperature with the addition of potassium ions. They also developed K^+-recognizable smart hydrogels for self-regulated controlled-release, which featured an isothermally K^+-induced pulse-release mode at a certain temperature due to the isothermally K^+-induced shrinking behavior of the hydrogel by recognizing the increase in the K^+ concentration in the environment. The selective formation of a stable 2:1 host–guest complex-

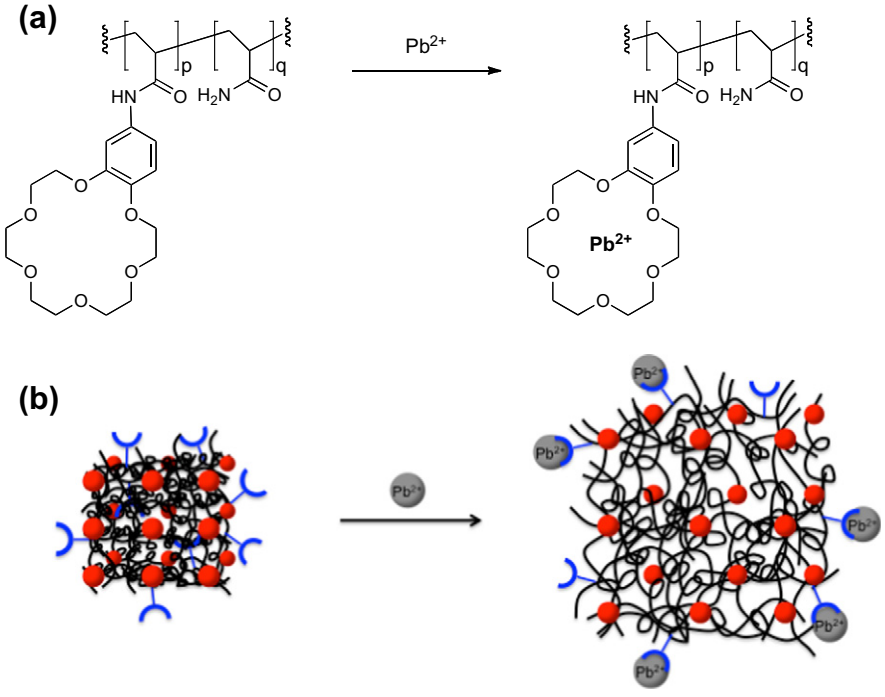

Fig. 3. (a) Chemical structures of stimuli-sensitive poly(acrylamide) gels with crown ether group and (b) a schematic illustration of swelling behavior of the polymer gel upon the addition of Pb^{2+}.

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