Thiourea-tagged poly(octadecyl acrylate) gels as fluoride and acetate responsive polymer gels through selective complexation†

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Fluoride and acetate-responsive polymer gels were prepared by incorporation of *p*-nitrophenylthiourea into poly(octadecyl acrylate) gels, and the colours and volumes were changed selectively in the presence of these ions by complexation in THF.

Stimuli-responsive polymer gels that can change their volumes drastically in response to various external physical and chemical stimuli have been of much interest due to various applications for actuators, drug delivery and microfluidic devices.[1–3] Among them, the stimuli-responsive polymer gels to specific chemical substances have been much studied due to application of molecular recognitions for material sciences.[4–10] However, they are mostly constructed by conjugation of receptors or host molecules with thermally-responsive hydrogels that undergo volume phase transitions in aqueous phase such as polyelectrolytes, proteins, or poly(NIPAM).[11–15] Thus, the guest molecules as the external stimuli have been still limited owing to difficulty in designing host–guest systems with high affinity in water.

Recently, we demonstrated that lipophilic polyelectrolyte gels bearing tetraalkylammonium tetraphenylborate had extraordinary high swelling abilities in non-polar organic solvents such as dichloromethane and THF.[16,17] They also exhibited discontinuous and drastic volume changes in response to changes of solvent polarities.[18] These results revealed that electrostatic repulsion and osmotic pressure among the dissociated ion pairs are readily useful in nonpolar media as driving force for volumetric changes of the polymer networks. This prompted us to design novel anion-responsive polymer gels peformed in nonpolar media by incorporation of anion receptors into the lipophilic polymer chain as schematically shown in Fig. 1. Complexation of specific anions with the receptors should enforce free counter cations to entrap in the inside of the polymer gels, which induces osmotic pressure and electrostatic repulsion to expand the gel. Non-polar media should allow us to use hydrogen bonds between the anion receptors and the target anions, which might increase binding affinity compared to that in water. Here, we demonstrate preparation of thiourea-tagged poly(octadecyl acrylate) gels and swelling behaviours in the presence of tetra(*n*-butyl)-ammonium salts with various anions shown in Fig. 2. A thiourea moiety was selected as the receptor site, because of remarkable binding abilities and colour changes to the specific anions such as fluoride and carboxylate by hydrogen bonds.[19–24]

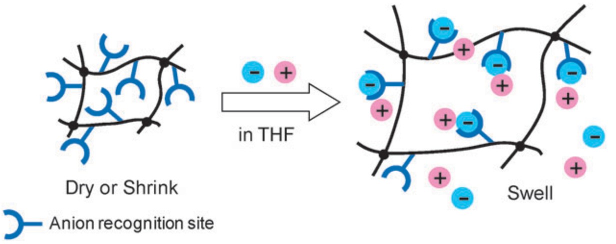

Fig. 1 Schematic illustration of an anion recognition gel.

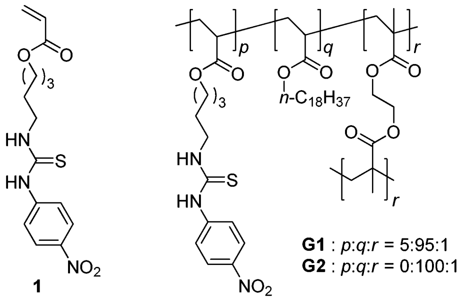

Fig. 2 Molecular structures of **1**, **G1** and **G2**.

Cross-linked poly(octadecyl acrylate) with a small amount of thiourea groups was prepared by radical copolymerization gelation from octadecyl acrylate (**ODA**), thiourea monomer **1** and ethylene glycol dimethacrylate (**EGDMA**) as a cross-linker in the presence of azobisisobutyronitrile (**AIBN**) as the initiator in the benzene–methanol mixture. The feed ratio was fixed at 95/5/1 for **ODA/1/EGDMA**. The formed gel (**G1**) was washed with methanol for 48 h, then air-dried at room temperature. The sample was cut into cylinders of about 1.0 mm in length and dried *in vacuo* at 40 °C. As a reference, cross-linked poly(octadecyl acrylate) without the thiourea moiety (**G2**) was prepared by the same procedure in the absence of **1**. The dried and cut gels were transferred into THF solutions of tetra(*n*-butyl)ammonium salt (**TBA**) with various concentrations and kept for 48 hours at room temperature for equilibrium swelling. Then, swollen gels were taken out from the solution and then weighted. Swelling degrees (Q) were calculated as the following equation:

$$Q = (W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}}\ (\text{wt/wt})$$

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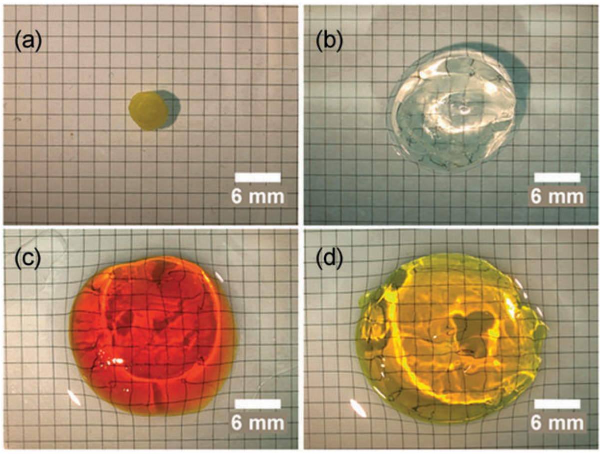

Fig. 3 Images of **G1**: (a) a dried gel, (b) a swollen gel in THF, (c) a swollen gel in THF in the presence of **TBA** fluoride (25 mM) and (d) **TBA** acetate (25 mM).

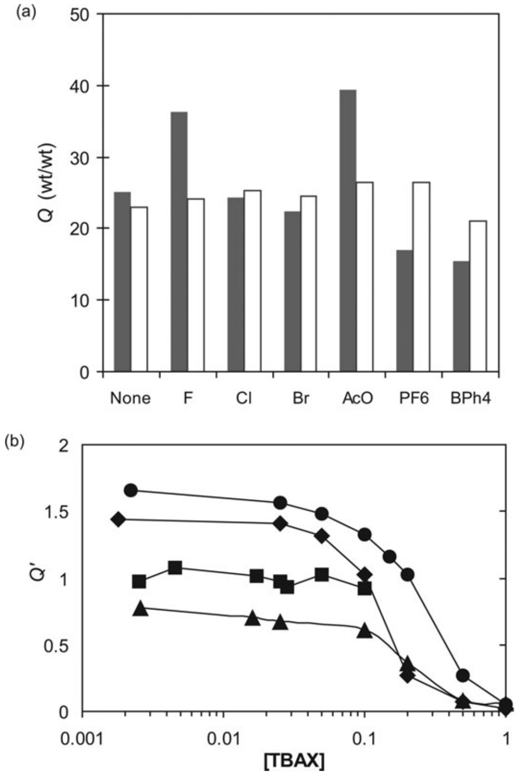

Fig. 4 (a) Swelling degrees (Q) of **G1** (grey bars) and **G2** (open bars) in the presence of **TBA** salts (25 mM) in THF. (b) The log plot of salt concentrations to relative swelling degrees (Q') of **G1** in the presence of various **TBA** salts in THF; (●) acetate, (◆) fluoride, (■) chloride, (▲) hexafluorophosphate anion.

where W_{wet} and W_{dry} are the weights of the dried gel and the wet gel, respectively.

A slightly yellow dried gel (**G1**) turned to be red and yellow-green by immersion in the THF solutions of the fluoride ion and acetate ion, respectively, as shown in Fig. 3. The colour changes occurred only in the solutions of these two anions, and other salts as well as salt-free THF remained colourless after swelling. This specific colour changes were attributed to complexation of *p*-nitrophenylthiourea moieties in the polymer chains with fluoride or acetate ions as the external stimuli. UV-vis titration experiments between the monomer **1** and acetate or fluoride in acetonitrile indicated that their binding constants (K) at 25 °C were 3.7×10^3 M^{-1} and 9.2×10^3 M^{-1} for fluoride and acetate, respectively. These values were similar in magnitude to those of the reported thiourea derivatives.[19,21] Then, we investigated the swelling behaviours of **G1** in the presence of various tetra(*n*-butyl)-ammonium salts at 25 mM (Fig. 4a).

In the fluoride and acetate solutions, the swelling degrees increased to about 40, compared to those in the salt-free solution ($Q_{\mathrm{o}} = 20$). On the other hand, in the bromide (Br) and chloride (Cl) solutions, they were nearly equal to those without salts. In the solution of more hydrophobic anions such as hexafluorophosphate ($\mathrm{PF_6}$) and tetraphenylborate ($\mathrm{BPh_4}$), they decreased to less than 20. Then, concentration dependence of the swelling degrees was investigated, and enhancement of the swelling degrees in the presence of **TBA** salts were estimated by relative swelling ratios; $Q' = Q/Q_{\mathrm{o}}$, where Q_{o} is the swelling degree of **G1** in salt-free THF, as shown in Fig. 4b. The swelling degrees were abruptly increased to their double on introduction of a fluoride or acetate anion. Then, the high swelling degrees were observed in the ranges with several ten millimolar and then they were gradually decreased with the increase in the anion concentrations. Since the estimated concentration of the thiourea groups in the polymer network of **G1** was 0.15 mmol g^{-1}, the binding of the external ions resulted in expansion of **G1**. The osmotic pressure and electrostatic repulsion might be generated by free moving tetra(*n*-butyl)ammonium counter cations in the polymer gels, and the swelling abilities should be further enhanced. However, in the presence of excess amount of the salts, the polarity of the media should increase with the increase in the salt concentration, and compatibility of the poly(octadecyl acrylate) to the solution decreases. Therefore, the swelling degrees decreased gradually. These effects were observed for concentration dependence of the swelling degrees in the presence of the ions that have no abilities to form complexes with the thiourea groups. In order to clarify the role of complexation, we tried removal of the fluoride anion from the red swollen gels ($Q = 40$) by soaking in a large volume of the THF mixture of methanol (8 : 2). After immersion for 48 hours at room temperature, the red gels collapsed and turned to be nearly colourless. The swelling degree decreased to 18, which was close to that of the swelling degree with salt-free THF. A few further cycles of alternative immersion in a 1 mM THF solution of **TBA** fluoride and THF–methanol (8 : 2) provided the alternative changes of swelling degrees and colour, as shown in Fig. 5. These results clearly indicate enhancement of swelling degrees by specific anions that can interact with the thiourea binding sites, and **G1** should be regarded as novel anion-responsive smart polymer gels with selective colour changes.

In conclusion, we demonstrate the fluoride or acetate anion-sensitive smart materials accompanied by the two changes of appearance of the polymer gels: their size and colour in the swelling state. Hence, they should be highly useful in an anion detecting and removing technology.

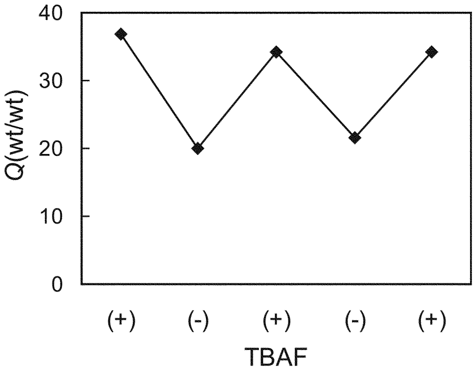

Fig. 5 Changes of swelling degrees of **G1**; (+) in 1 mM THF solutions of **TBA** fluoride and (−) in the THF–methanol mixture (8 : 2).

Although the swelling behaviours of ion-sensitive hydrogels have been well documented in aqueous solutions,[9,10] our system lays on the reliable molecular recognition of thiourea for specific anions with the aid of hydrogen-bonded complexation in nonpolar media. Our result suggests that drastic volumetric change of polymer gels should be acquired by increase of osmotic pressure by entrapping external guest molecules, which should be a powerful tool for designing guest-responsive smart materials. Moreover, utility of the non-polar media enables us to use a library of well-defined hydrogen-bonded host–guest systems in supramolecular chemistry for their designs.[25–27] Preparation and swelling abilities of various guest-responsive polymer gels are under current investigation.

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