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COMMUNICATION

Reversible water uptake/release by thermoresponsive polyelectrolyte hydrogels derived from ionic liquids

Cite this: DOI: 10.1039/x0xx00000x

Yuki Deguchi,^{a,b} Yuki Kohno^{b,c} and Hiroyuki Ohno^{*,a,b}Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Thermoresponsive polyelectrolyte hydrogels, derived from tetra-*n*-alkylphosphonium 3-sulfopropyl methacrylate-type ionic liquid monomers, show reversible water uptake/release, in which the gels absorb/desorb water for at least ten cycles via a lower critical solution temperature-type phase transition.

Ionic liquids (ILs) are organic salts with melting points below 100 °C, and have attracted a keen attention as a new type of liquid-state materials due to their unique physico-chemical properties such as negligibly low vapour pressure, liquid state in the wide range of temperature, and high charge density.¹ In 1998, we first reported IL-based polyelectrolytes (*i.e.*, poly(ionic liquids); PILs), where component ions of ILs were covalently bound onto macromolecular architecture.² Most interesting property of these PILs is their very low glass transition temperature as compared with that of conventional polyelectrolytes. Studies on these PILs have received attention because of their capability to show the IL-based properties, which make them different from any classical polyelectrolytes.

Most of the studies on PILs have been focused on the design, preparation, and characterisation of neat-state PILs for solid-state electrolytes.³ On the other hand, mixtures of PILs and other molecular solvents, in particular water, have recently emerged as an interesting materials. Through comprehensive studies on the temperature-dependent compatibility of ILs with water,⁴ adequate hydrophobicity of the ion pair was found to be an essential factor to realise a lower critical solution temperature (LCST)-type phase behaviour after mixing the ILs with water.^{4f} Based on this basis, it was not difficult for us to design thermoresponsive polyelectrolytes. Our group and Yuan's group independently reported several PIL/water mixtures that show the LCST-type phase behaviour.⁵ Distinct from well-known non-ionic polymers showing the LCST-type phase transition, *e.g.*, poly(*N*-isopropylacrylamide), the reported thermoresponsive PILs offer potential capabilities to provide functional interfaces especially for separation, stabilisation, and condensation of charged molecules, achievable by suitable combination of highly charged character of ILs and highly sensitive thermoresponsiveness.⁶

Fabrication of various solid-state materials, *e.g.*, membranes, nanoparticles, and gels made from these thermoresponsive PILs, is one of the effective strategies to expand the possibility of the thermoresponsive PILs as functional interfaces. A few studies have recently been reported in the design of cross-linked thermoresponsive PIL hydrogels. Diamond's group prepared PIL-based hydrogels by the polymerisation of tetrabutylphosphonium styrenesulfonate ([P₄₄₄₄][SS]) and tributyl-*n*-hexylphosphonium 3-sulfopropyl acrylate ([P₄₄₄₆][AC3S]).⁷ We also prepared PIL hydrogels using 3-sulfopropylmethacrylate-based IL monomers paired with [P₄₄₄₆]⁺ cation ([P₄₄₄₆][MC3S]) or tributyl-*n*-octylphosphonium cation ([P₄₄₄₈][MC3S]).⁸ Yuan and co-workers reported a gemini-type dicationic phosphonium-based hydrogel with [SS]⁻ as an anion.⁹ Some of these PIL gels shrunk upon elevating temperatures, which clearly indicated that the LCST-type thermoresponsiveness was maintained even after gelation of the PILs. In addition, we reported that the prepared copolymer-type poly([P₄₄₄₆][MC3S]-*co*-[P₄₄₄₈][MC3S]) hydrogels underwent desorption of water upon mild heating of the hydrogel.⁷ The reported PIL hydrogels, however, were still fragile and accordingly their mechanical properties were not good enough for reversible water absorption/desorption.

This paper aims to investigate necessary conditions to prepare PIL hydrogels that reversibly undergo water uptake/release, that is, absorb/desorb water *via* the LCST-type phase transition, while maintaining their mechanical properties. Through careful selection of both initiators and cross-linkers, as well as reaction procedures, we have prepared a few mechanically-stable thermoresponsive PIL hydrogels that reversibly absorb/desorb water molecules by moderate temperature change. In spite of some papers on a small number of thermoresponsive PILs showing LCST-type phase behaviour, to our knowledge, there is no report on a PIL hydrogel that endures repeating cycles of thermoresponsive water uptake/release.

Table 1 summarises both components to prepare PIL hydrogels and results of water absorption/desorption reversibility of the prepared hydrogels upon temperature change. We preliminarily sought appropriate initiators and cross-linkers for gelation of [P₄₄₄₆][MC3S]. Five cross-linkers were chosen, *i.e.*,

Table 1 The synthetic condition and water absorption/desorption reversibility of thermoresponsive PIL hydrogels

Entry	Cross-linker ^a	Initiator ^b	Water uptake/release reversibility
<u>1</u>	EGDM	AIBN	– ^c
<u>2</u>	TEGDM	AIBN	–
<u>3</u>	C ₆ DM	AIBN	–
<u>4</u>	C ₁₄ DM	AIBN	–
<u>5</u>	PEGDM	AIBN	+ ^d
<u>6</u>	PEGDM	APS/TEMED	–
<u>7</u>	PEGDM	VA-046B	+

^aThe concentration of cross-linkers was 1.0-3.0 mol% for EGD, TED, C₆M, and C₁₄M, and that was 0.1 mol% for PEGDM to IL monomer. ^bThe concentration of each thermal initiator was 0.1 mol% for both AIBN and VA-046B, and 0.3-0.4 mol% for APS/TEMED to IL monomer.

^cThese gels were fragile and did not show reversible absorption/desorption of water; ^dThese gels absorbed and desorbed water

ethylene glycol dimethacrylate (EGDM), triethylene glycol dimethacrylate (TEGDM), 1,6-hexylene dimethacrylate (C₆DM), 1,14-tetradecanediol dimethacrylate (C₁₄DM), and poly(ethylene glycol) dimethacrylate with the number-average molecular weight of 550 (PEGDM). As for initiators of free radical polymerisation, we used 2,2'-azobis(isobutyronitrile) (AIBN), ammonium persulfate (APS) with tetramethylethylenediamine (TEMED), and 2,2'-azobis[2-(2-imidazolin-2-yl)propane]disulfate dihydrate (VA-046B). Structure of these IL monomers, cross-linkers, and free radical initiators is summarised in Figs. S1, S2 and S3 (ESI). Both [P₄₄₄₆][MC3S] and pure water were mixed to reach monomer concentration of 70 wt%, then each cross-linker was added to this mixture up to the concentration of 3 mol% to the IL monomer. The resulting mixtures were individually placed into a vial for samples from 1 to 5 or a disposable syringe for 6 and 7. These were degassed by ultrasonication, and a free radical initiator was then dissolved in the mixture, and sealed under N₂ atmosphere. To induce gelation, the mixtures were heated up to 80 °C for 1 to 5, and 50 °C for 7, depending on the initiators. In the case of APS/TEMED system, 6, the polymerisation was carried out at room temperature. After gelation, the resulting PIL hydrogels were peeled off from the containers, and soaked in pure water. After equilibrium soaking of water into the hydrogel, the visual appearance of the resulting PIL hydrogels was confirmed. Temperature-dependent water uptake/release behaviour was further investigated by heating the gels to induce the LCST-type phase transition only when they showed no crack after water absorption.

The effect of cross-linkers on the stability of the PIL hydrogels was investigated, where AIBN was used as an initiator (entry 1 to 5). Both EGDM and TEGDM with relatively short spacer made the hydrogel fragile and stiff. The gels showed complete fragmentation when soaking them in pure water. On the other hand, the PIL hydrogels prepared with C₆DM and C₁₄DM were stable and did not undergo fragmentation after soaking in pure water. However, once these PIL hydrogels were heated to induce the LCST-type phase transition, they were fragmented after water desorption. Relatively stable PIL hydrogels showing reversible water uptake/release behaviour were prepared when PEGDM having sufficiently long ethylene glycol spacer was used as a cross-linker (entry 5). Temperature-dependent water content and time-dependent

absorption amount of water of the PIL gel were then determined (see Figs. S4 and S5 in ESI). The PIL hydrogel reversibly absorb/desorb water upon temperature change, but after absorption/desorption cycling for four or five times, the hydrogel was fragmented.

In general, the radical source itself does not significantly affect the structure of the resulting gels. On the other hand, we anticipate that the homogeneity/heterogeneity of the reaction mixtures during the polymerisation significantly influences the structure of the gels. As [P₄₄₄₆][MC3S] shows LCST behaviour with water,^{5c} the monomer was phase-separated from water at relatively high temperature at which AIBN was effectively initiate the polymerisation. The polymerisation therefore proceeded under heterogeneous condition. Such heterogeneous gelation reaction was also exploited for gemini-dicationic PIL systems by Yuan's group.⁹ Although there were still no detailed data on the mechanical properties of the gels upon temperature change, the heterogeneity of the reaction mixtures was considered to make these hydrogels fragile.

AIBN was then replaced by two different initiators such as APS/TEMED and VA-046B for radical polymerisation at low-temperature, so that the polymerisation was carried out under homogeneous condition. The PEGDM-type cross-linker was used in all the following systems because it provided relatively stable PIL hydrogels. The gelation was undertaken at room temperature and 50 °C for APS/TEMED system and VA-046B system, respectively. Up to 50 °C, the reaction mixture remained homogeneous. When APS/TEMED was applied (entry 6), the resulting mixture was still liquid phase and did not undergo gelation regardless of the initiator concentration tested. By contrast, a mechanically-stable, transparent, and thermoresponsive PIL hydrogel was obtained by employing VA-046B (entry 7). No vinyl groups were confirmed in ATR-FTIR spectra of the gels (Fig. S6). Detailed investigations were then undertaken for PIL hydrogels prepared by this method (entry 7).

We have already reported that the phase transition temperature (T_c) of the thermoresponsive PILs was finely tuned by copolymerisation of IL monomers with different hydrophobicity, and introduction of a bit more hydrophobic IL monomers lowered the T_c value.^{5c,8} We then prepared copolymer-type hydrogels composed of [P₄₄₄₆][MC3S] and more hydrophobic [P₄₄₄₈][MC3S] *via* the same condition as for entry 7. The prepared hydrogels were denoted as poly((P₄₄₄₆)[MC3S]_x-co-(P₄₄₄₈)[MC3S]_{1-x}), where x corresponds to the molar fraction of the IL monomer [P₄₄₄₆][MC3S]. Four distinct hydrogels with different x values from 1.0 to 0.4 were prepared in this study. The T_c values of the PIL hydrogels were previously determined from typical endothermic peak in the DSC chart during the LCST-type phase transition.⁸ Such an endothermic peak was seen in a PIL hydrogel prepared by a method, entry 5 (Fig. S7 in ESI). However, no endothermic peaks were detected for PIL hydrogels prepared by a method, entry 7 presumably because of high water content in the hydrogels (> 99 wt%). Instead, the phase transition was visually confirmed by detecting turbidity change of the hydrogels upon heating. We tentatively assigned the temperature at the transparent-to-turbid transition as the T_c . The T_c value lowered upon decreasing the x value (see Table S1 in ESI); this correlation between the hydrophobicity of IL monomers and T_c value was consistent with our previous studies.⁴

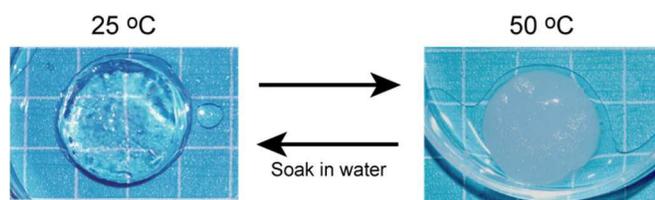


Fig. 1 Photograph of poly([P₄₄₄₆][MC3S]_{0.5}-co-[P₄₄₄₈][MC3S]_{0.5}) hydrogel prepared under the condition of entry 7, showing reversible water uptake/release upon moderate temperature change.

Photograph in Fig. 1 shows thermoresponsive water uptake/release behaviour of poly([P₄₄₄₆][MC3S]_{0.5}-co-[P₄₄₄₈][MC3S]_{0.5}) hydrogel. The hydrogel was apparently transparent at 25 °C (Fig. 1, left), and it turned turbid at 30 °C (T_c of this gel). Further increase in temperature induced desorption of water from the hydrogel, and eventually the hydrogel shrank (Fig. 1, right at 50 °C). Temperature-dependent water content of the gel was summarised in ESI (Fig. S8). The gel was found to absorb water by soaking the hydrogel in pure water at temperature below the T_c (Fig. S9 in ESI). No fragmentation was found in the hydrogel during the re-absorption of water.

Next, we examined reversibility of water uptake/release by poly([P₄₄₄₆][MC3S]_{0.5}-co-[P₄₄₄₈][MC3S]_{0.5}) hydrogels. The as-prepared hydrogel was soaked in pure water for 2.5h at 5 °C to reach the equilibrium absorption of water, and placed the hydrogel in a chamber, kept at 50 °C, for 30 min to desorb water. This absorption/desorption process was repeated for ten times in this study. The water content of the PIL hydrogel was determined by measuring weight of water-saturated gel ($W_{\text{water+polymer}}$) and dry gel (W_{polymer}), according to the following eq. 1;

$$\text{Water content of gel} = (W_{\text{water+polymer}} - W_{\text{polymer}}) / W_{\text{polymer}} \quad (\text{eq. 1})$$

Fig. 2 summarises the change of the water content of poly([P₄₄₄₆][MC3S]_{0.5}-co-[P₄₄₄₈][MC3S]_{0.5}) gels by temperature cycling. The water content of the water-saturated hydrogel was 280. this value was approximately 28 times higher than that of the previously reported PIL hydrogel.⁸ The hydrogel oozed a considerable amount of water at 50 °C. The average water content was calculated to be 242 after desorption at 50 °C. The gel oozed more water by further heating, but we have analysed the

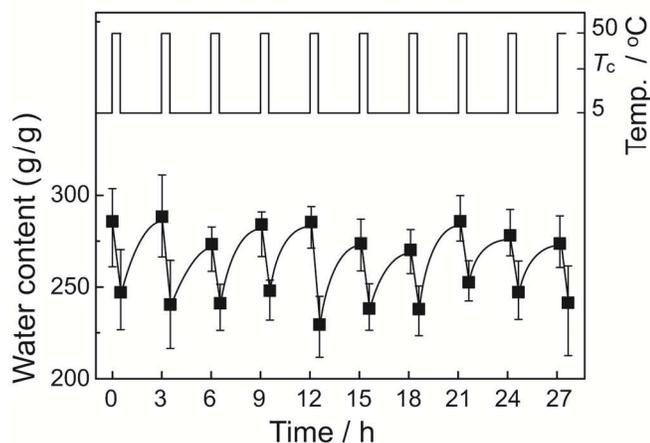


Fig. 2 Thermoresponsive and reversible water uptake/release by poly([P₄₄₄₆][MC3S]_{0.5}-co-[P₄₄₄₈][MC3S]_{0.5}) hydrogel upon temperature change.

reversibility of water uptake/release at temperature between 5 and 50 °C. This hydrogel was found to be stable without generating any crack even after absorption/desorption cycles for ten times. It can be claimed, therefore, that suitably prepared PIL hydrogels in this study is able to undergo reversible water uptake/release without degradation. The water content in the hydrogel was sometimes fluctuating, which resulted in rather large error bars as shown in Fig. 2. Before measuring the water content of the hydrogel, we needed to wipe off the excess amount of the oozed water on the gel. This process might be a reason for the fluctuation. Optimisation of the analytical procedures is now under way. Since an increasing number of intriguing papers have recently been reported on thermoresponsive PILs,¹⁰ our results of water uptake/release mentioned here would provide a new platform to fabricate a wide variety of solid-state materials based on these PILs.

Conclusions

A new type of cross-linked, thermoresponsive PIL hydrogel showing LCST behaviour has been prepared by utilising adequate IL monomer, cross-linker, and radical polymerisation initiator. Thus prepared hydrogels reversibly absorb/desorb water by a small temperature change.

Financial support for this work was provided by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (KAKENHI, No. 26248049). Y.K. acknowledges the Japan Society for the Promotion of Sciences for financial support (Postdoctoral Fellowship for Research Abroad).

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^aDepartment of Biotechnology, Tokyo University of Agriculture and Technology, Naka-cho, Koganei, Tokyo 184-8588, Japan. Tel and FAX: +81-42-388-7024, E-mail: ohnoh@cc.tuat.ac.jp

^bFunctional Ionic Liquid Laboratories, Graduate School of Engineering, Tokyo University of Agriculture and Technology, Naka-cho, Koganei, Tokyo 184-8588, Japan

^cDept. of Chemical & Biological Engineering, University of Colorado, Boulder, CO80309, USA

Electronic Supplementary Information (ESI) available: Synthetic procedure and characterisation data for IL monomers, and structure of cross-linkers and initiators. See DOI: 10.1039/x0xx00000x

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