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Design of thermoresponsive poly(ionic liquid) gels containing proline units to catalyse aldol reaction in water

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ABSTRACT

Ionic liquid monomers and a proline-containing monomer were copolymerised in the presence of cross-linker to form ionic liquid polymer gels that show lower critical solution temperature-type phase change in water. The obtained gels were utilised as catalysts for aldol reaction in water. Since proline-catalysed aldol reaction is composed of three equilibrium steps including dehydration condensation reaction and hydrolysis reaction, yield of product was affected by the water content around the proline unit in the gel. Since thus prepared ionic liquid polymer gels showed the thermo-responsive change in water content, the product yield was found to be affected by the temperature around the phase transition temperature.

1. Introduction

Some ionic liquids (ILs) were found to show a lower critical solution temperature (LCST)-type phase change after mixing them with water [1–9]. Systematic studies done by Kohno et al. revealed that LCST behavior of IL/water mixtures was seen in ILs having finely balanced hydrophobicity/hydrophilicity [3–5]. These ILs were prepared by the combination of cations and anions to show moderate hydrophobicity, as confirmed by hydrophilicity index value [5]. The transition temperature between miscible state and immiscible state of IL/water mixtures was also controlled by the hydrophobicity/hydrophilicity balance of the ion structures [1,3,5–9]. This phase transition is comprehended as change in hydration degree of the component ions. It is interesting that these ILs can be polymerised after introducing polymerisable groups on the charged sites, and thus obtained polymerised ILs also show the LCST-type phase change in water [10–17]. Similar to non-polymerised ILs showing the LCST behavior, the total hydrophobicity/hydrophilicity balance of the IL monomers was the major factor to govern the transition temperature of the resulting polymerised ILs. Accordingly, the transition temperature was freely controlled by the copolymerisation of IL monomers with different hydrophobicity [10,11]. Significant change in hydration degree was also detected as temperature-dependent and reversible water absorption/desorption behavior in chemically cross-linked IL polymer gels (IL gels) derived from the IL monomers [18–26]. This study enabled to provide IL gels having ability to pump water by small temperature change [19,21]. We have also tried to pump pure water from sea water with the IL gels, but the salt concentration was found to considerably affect the thermal response [21]. In spite of the limited number of examples as mentioned above, there are a wide range of potential applications with these thermo-responsive IL gels. Little reports exist on the dynamic change in water content of the IL gels driven by a small temperature change.

In the present paper, we have focused on the proline-catalysed aldol reaction [27–30]. Proline-catalysed aldol reaction is known to be composed of three steps. Among these, there are two steps that water plays a key role, i.e., initial dehydration condensation reaction and subsequent hydrolysis reaction [31,32]. These steps are susceptible to water content in the reaction system. Accordingly, the yield of products depended on the hydrated state around the proline moiety. Addition of water into the system containing small amount of water should be good to obtain high product yield for one-pot reaction systems. However, strict and reversible control of water content in the systems should be required for entire catalytic cycling steps. Our challenge is to evaluate the effect of water content on the overall reaction yield of proline-catalysed aldol reaction with the aid of IL gels showing the LCST-type phase change.

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2. Experimental section

2.1. Materials

Tributylphosphine (>95.0% purity), sodium 1-pentane sulfonate (>98.0% purity), 4-chloromethylstyrene (>95.0% purity), *trans*-4-hydroxy-L-proline (>99.0% purity), trifluoroacetic acid (>99.0% purity), acryloyl chloride (>98.0% purity), and 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (>98.0% purity) were purchased from Tokyo Chemical Industry Co. Polyethylene glycol (PEG) dimethacrylate (average $M_n = 550$), cyclohexanone (>99.8% purity), and *p*-nitrobenzaldehyde (>99% purity) were purchased from Sigma-Aldrich Co. Diethyl ether (>99.0% purity), acetonitrile (>99.0% purity), and chloroform (>99.0% purity) were purchased from Kanto Chemical Industry Co. Tripentylphosphine of reagent grade was donated from Hokko Chemical Industry Co. Milli-Q (EMD Millipore) was used for all experiments in this study. All of the chemicals and solvents were used as received otherwise mentioned.

2.2. Monomer synthesis

Fig. 1 shows the structure of IL monomers and proline monomer. Tributyl(vinylbenzyl)phosphonium chloride [33], tripentyl(vinylbenzyl)phosphonium chloride [21], tributyl(vinylbenzyl)phosphonium 1-pentanesulfonate (P4) [12], and *trans*-4-(acryloyloxy)-L-proline hydrochloride [34] were prepared according to the previously reported procedures. As for the preparation of tripentyl(vinylbenzyl)phosphonium 1-pentane sulfonate (P5), both tripentyl(vinylbenzyl)phosphonium chloride (4.21 g, 10.6 mmol) and sodium 1-pentane sulfonate (2.37 g, 13.7 mmol) were mixed in water (50 ml) and stirred for overnight at room temperature. Chloroform (200 ml) was then added in the solution and the organic layer was washed several times with water (50 ml) until no AgCl precipitate was found by silver nitrate test. Chloroform was removed by evaporation to give P5 as a white solid (5.1 g, 94%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.39(d, $J = 8.4$ Hz, 2 H), 7.34 (dd $J = 8.4$ Hz, $J = 2.4$ Hz, 2 H), 6.68 (dd $J = 17.9$ Hz, $J = 11.2$ Hz, 1 H), 5.76 (d $J = 17.2$ Hz, 1 H), 5.30 (d $J = 11.0$ Hz, 1 H), 4.03 (d $J = 15.1$ Hz, 2 H), 2.87 (t $J = 8.29$ Hz, 2 H), 2.28–2.36 (m, 6 H), 1.84–1.93 (m, 2 H), 1.27–1.51 (m, 22 H), 0.89 (t, $J = 8.29$ Hz, 12 H).

2.3. Preparation of ionic liquid gels

Both homopolymer-type IL polymer gel using P4 as a monomer (PP4) and copolymer-type IL polymer gels composed of P4, P5, and proline monomer with different molar fractions (P(P4$_x$-*co*-P5$_{(0.9-x)}$-*co*-pro$_{0.1}$) with x value ranging from 0 to 0.9) were prepared according to our previous reports with modification [18–21]. IL monomers (P4 and P5), *trans*-4-(acryloyloxy)-L-proline hydrochloride, PEG dimethacrylate (cross-linker), and 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (radical initiator) were mixed with a molar ratio of 90/10/1/1, and further mixed with water (water content: 10 wt%). The mixture was vortexed and warmed gently up to it reached a homogenous solution. After degassing by sonication, the solution was sandwiched with two quartz plates containing a 120-μm-thickness spacer. This was then irradiated with 365 nm light (2.3 mW cm^{-2}) for 1 h at room temperature. The obtained IL gels were soaked in triethylamine aq. soln. to neutralise hydrochloric acid, then soaked in pure water to remove the resulting salts, excess triethylamine, and unreacted monomers if any. FT-IR spectra of the monomers and obtained gels revealed the completion of polymerisation (Fig. S1). Swelling degree of thus obtained IL gels was evaluated according to the method reported in our previous papers [18–21].

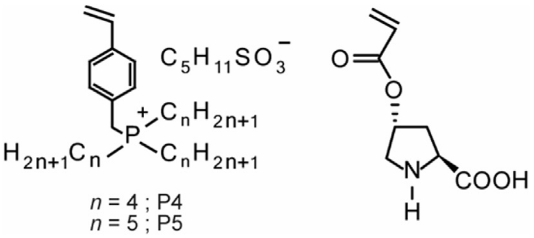

Fig. 1. Structure of IL monomers Pn (n = 4 or 5) (left) and proline monomer (right).

2.4. Proline-catalysed aldol reaction

Thermoresponsive IL gels (TPIL gels), *p*-nitrobenzaldehyde (10 eq. to proline unit), cyclohexanone (70 eq. to proline unit) were dispersed in water (0.2 ml per 1 mg of TPIL gels). The dispersed aq. soln. was stirred (290 rpm) at the desired temperature to carry out the reaction. It was hard to extract the residual compounds in TPIL gels during the reaction. Instead, small amount of the aqueous phase was removed by a pipette at scheduled time intervals. $CDCl_3$ was added to the pipetted aqueous solution to extract both product (2-(hydroxy(4-nitrophenyl)methyl)cyclohexanone) and substrates, and the $CDCl_3$ layer was then analysed with ^{1}H NMR spectroscopy. With the signal intensity ratio in the ^{1}H NMR chart, conversion efficiency of the product was calculated according to the following equation (1) [35,36].

$$\text{Conversion efficiency (\%)} = [I_{7.5}/(I_{7.5} + I_{8.0})] \times 100 \qquad (1)$$

where $I_{7.5}$ and $I_{8.0}$ denotes the integrated intensity of a signal at 7.46–7.52 ppm (for 2-(hydroxy(4-nitrophenyl)methyl)cyclohexanone) and 8.05–8.09 ppm (for *p*-nitrobenzaldehyde), respectively. Typical ^{1}H NMR spectrum after the proline-catalysed aldol reaction is shown in Fig. S2.

3. Results and discussion

3.1. Thermal phase behavior of proline-functionalised IL gels

First, we have examined the effect of temperature on the swelling degree of PP4 gel. The swelling degree of gels was defined here to be the weight ratio of absorbed water and the gel. Large swelling degree means well-hydrated condition of the gels. The swelling degree of PP4 gel was 12.8 at 10 °C, and it gradually decreased with heating. It dropped at around 50 °C to reach 2.9 at 60 °C as shown in Fig. 2. As shown in this figure, considerable change of the swelling in the gel by a small temperature change such as from 50 to 60 °C. This large change in the water content is one of excellent properties of the TPIL gels. The transition temperature of IL gels is affected by some factors such as hydrophobicity of IL monomer, copolymerisation with other IL monomers having different hydrophobicity, and so on. In the present paper, we have examined the TPIL gels obtained by the polymerisation under the composition as mentioned in the experimental section.

Then we examined the swelling profile of proline containing IL gel. The IL gel containing both P4 monomer and proline monomer (P(P4$_{0.9}$-*co*-pro$_{0.1}$)) was examined by the same method as mentioned above. The swelling degree of P(P4$_{0.9}$-*co*-pro$_{0.1}$) gel was 14.9 at 10 °C, but there was no drastic change in the swelling property. High swelling degree was maintained even after heating, and the degree was 11.7 at 70 °C.

As mentioned above, the transition temperature was controllable by a few factors. This less temperature sensitive properties can