Electronic Supplementary Information

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

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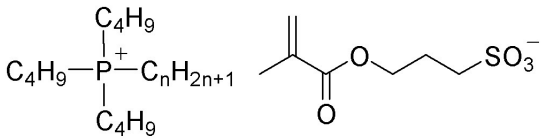
1. Materials and Instrumentation

Tributyl-*n*-hexylphosphonium bromide ([P_{4446}]Br) was donated from Hokko Chemical Industry Co. Tributyl-*n*-octylphosphonium bromide ([P_{4448}]Br), ethylene glycol dimethacrylate (EGDM), triethylene glycol dimethacrylate (TEGDM), and potassium 3-sulfopropylmethacrylate (K[MC3S]) were purchased from Tokyo Chemical Industry Co. 1,6-hexylene dimethacrylate (C_6DM), 2,2'-azobis[2-(2-imidazolin-2-yl)propane]disulfate dehydrate (VA-046B), and ammonium persulfate (APS) were purchased from Wako Chemical Industry Co. 1,14-tetradecanediol dimethacrylate (C_{14}DM) and poly(ethylene glycol) dimethacrylate with the number-average molecular weight of 550 (PEGDM) were purchased from Sigma-Aldrich Co. 2,2'-Azobis(isobutyronitrile) (AIBN) tetramethylenediamine (TEMED) were purchased from Kanto Chemical Co. AIBN was recrystallised with ethanol prior to use. All of the other chemicals and solvents were used as received for synthesis. [P_{4446}][MC3S] and [P_{4448}][MC3S] were prepared according to our previous report.[1] Differential scanning calorimetry (DSC) was performed with a DSC-6220 instrument (Seiko Instruments Inc.) at a heating rate of 5 °C min^{-1}. Attenuated total reflectance (ATR)-FTIR measurement was performed with JASCO FT/IR 4200, ATR PRO410-S.

Reference

1 Y. Deguchi, Y. Kohno and H. Ohno, *Aust. J. Chem.*, 2014, **67**, 1666.



n = 6; $[P_{4446}][MC3S]$
n = 8; $[P_{4448}][MC3S]$

Fig. S1 Structure of IL monomers.

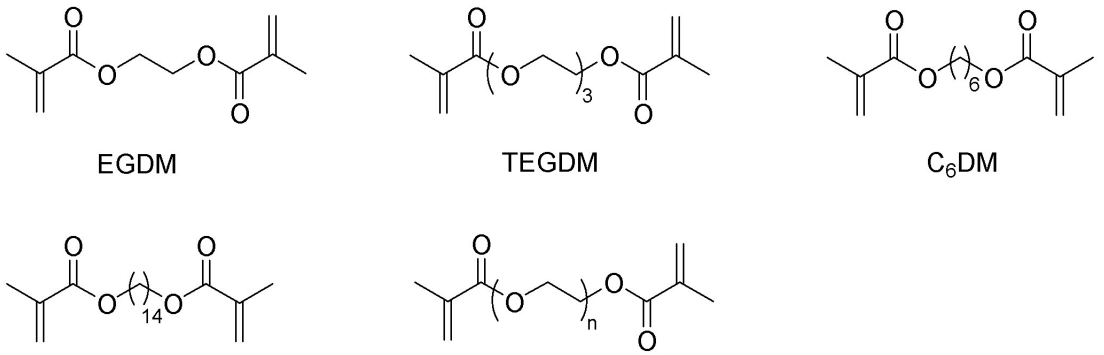


Fig. S2 Structure of cross-linkers.

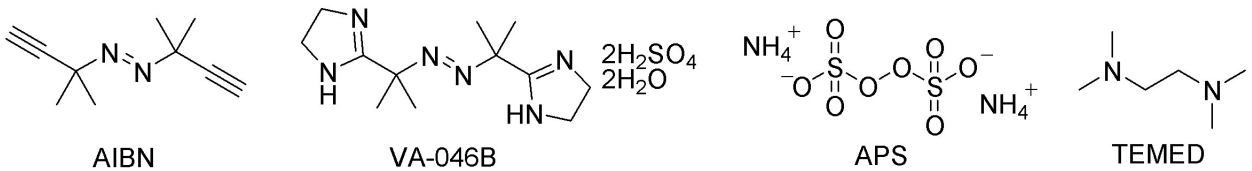


Fig. S3 Structure of radical initiators.

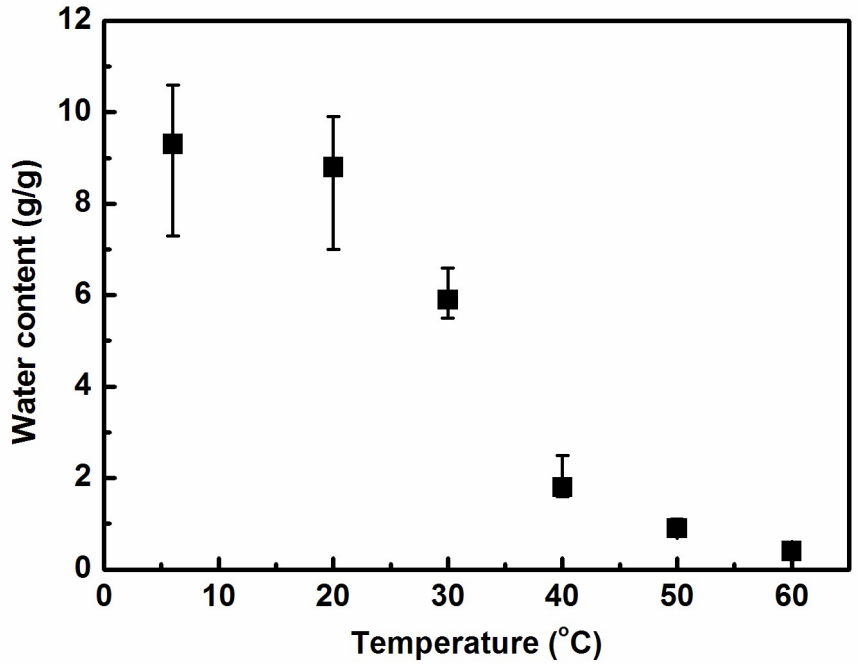


Fig. S4 The water content (g/g) of poly([P_{4446}][MC3S]$_{0.6}$-*co*-[P_{4448}][MC3S]$_{0.4}$) gel prepared by a method, entry **5** upon temperature change. The water content was determined after storing the gel in a chamber at each temperature for 30 min.

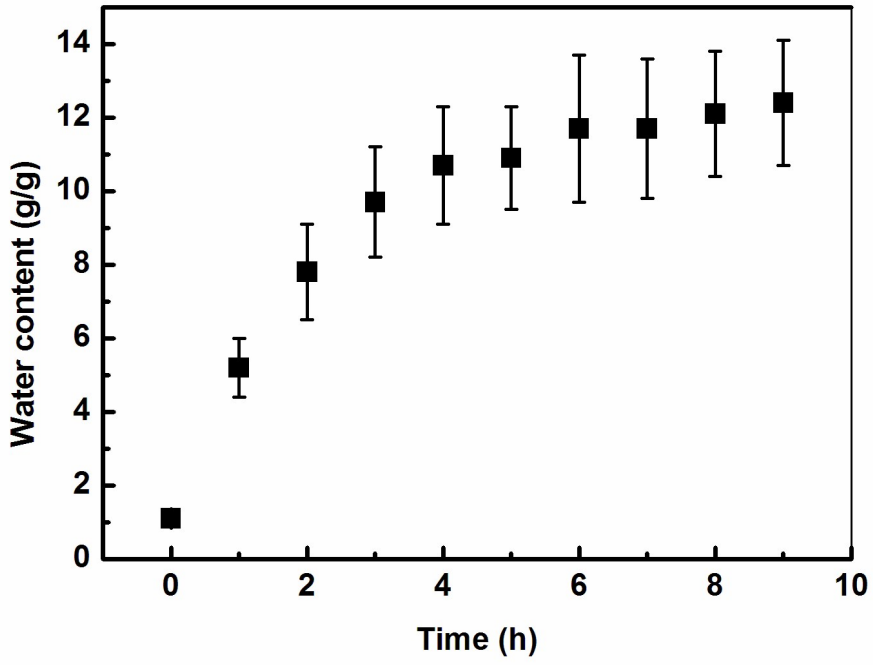


Fig. S5 Time-dependent water content (g/g) of poly([P_{4446}][MC3S]$_{0.6}$-*co*-[P_{4448}][MC3S]$_{0.4}$) gel prepared by a method, entry **5** at 5 °C after desorption of water *via* the LCST behaviour.

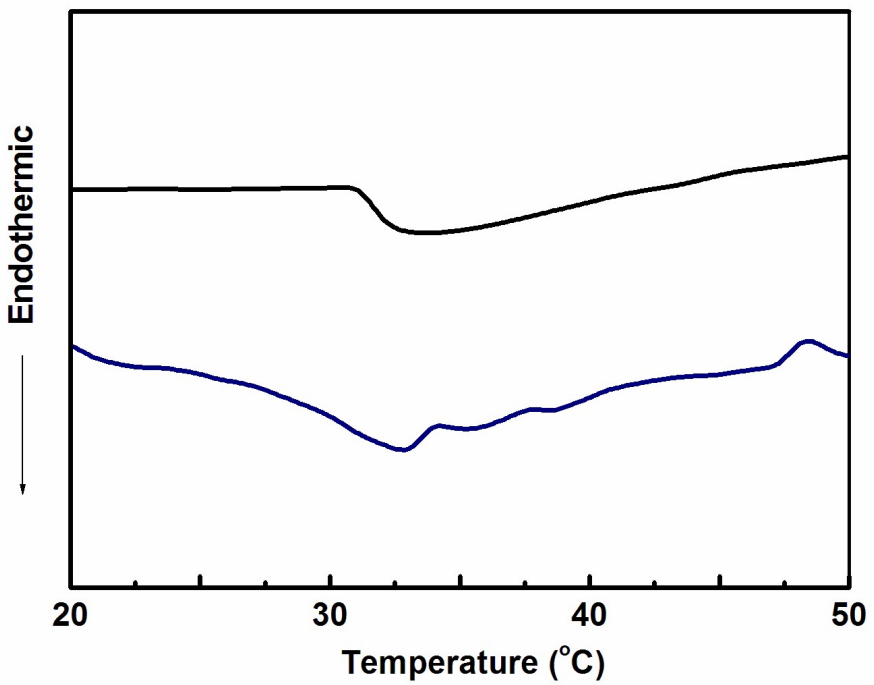


Fig. S6 DSC profile of poly([P_{4446}][MC3S]$_{0.6}$-*co*-[P_{4448}][MC3S]$_{0.4}$) linear polymer (black line) and poly([P_{4446}][MC3S]$_{0.6}$-*co*-[P_{4448}][MC3S]$_{0.4}$) gel prepared by a method, entry **5** (blue line).

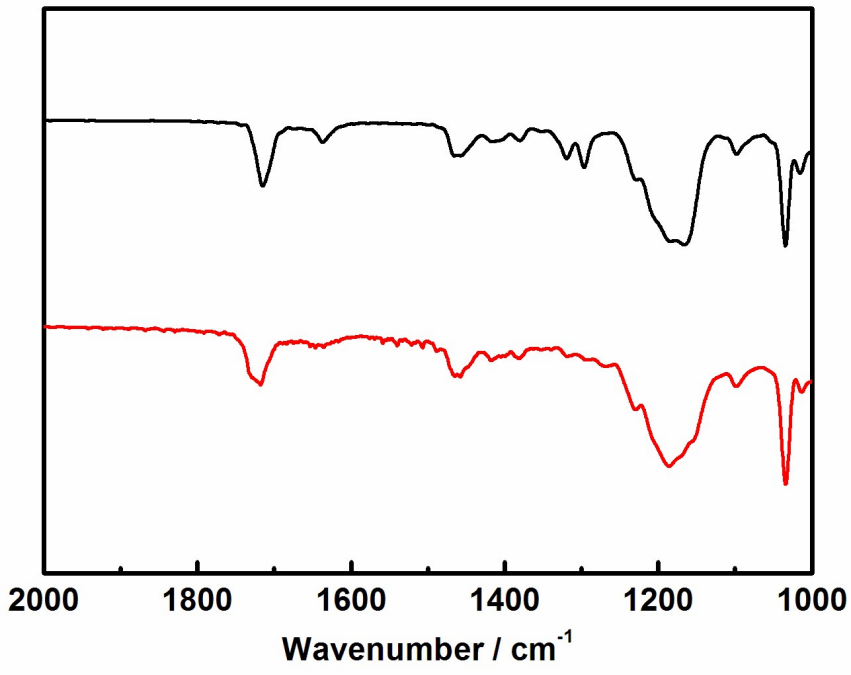


Fig. S7 ATR-FTIR spectra of [P_{4446}][MC3S] (black line) and poly([P_{4446}][MC3S]) gel prepared by method, entry **7** (red line).

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Table S1 The visually-confirmed T_c values of poly([P_{4446}][MC3S]$_x$-*co*-[P_{4448}][MC3S]$_{1-x}$) gel prepared by a method, entry 7, where x value corresponds to the mole fraction of [P_{4446}][MC3S]

x	T_c (°C)
1.0	65
0.8	55
0.6	35
0.5	30
0.4	30

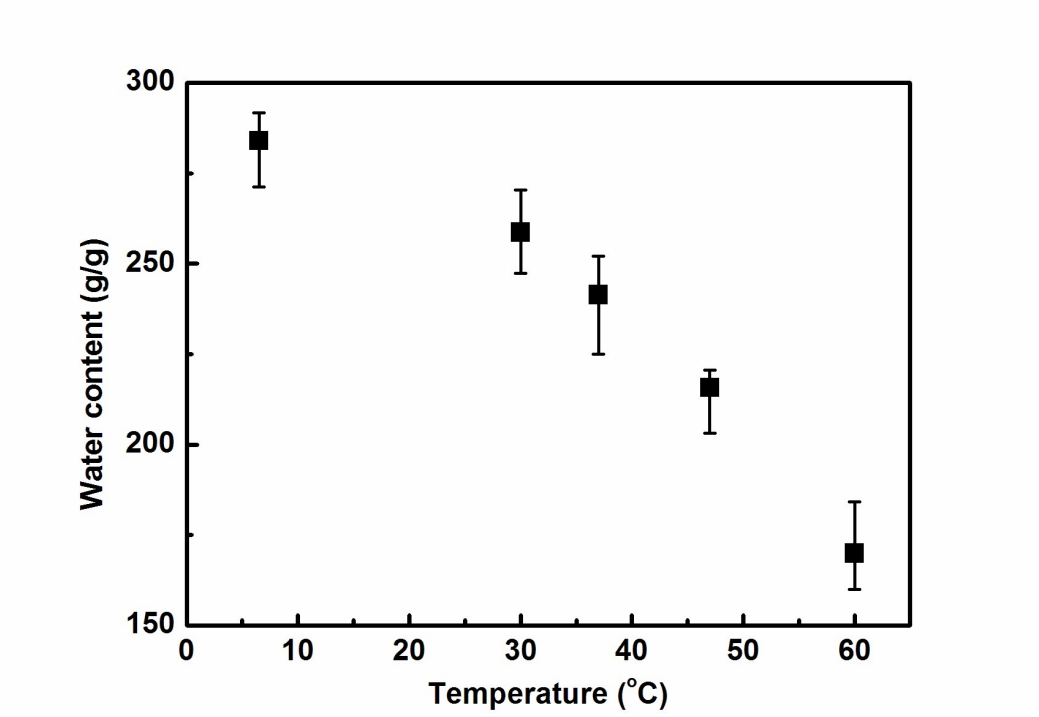

Fig. S8 The water content (g/g) of poly([P_{4446}][MC3S]$_{0.5}$-*co*-[P_{4448}][MC3S]$_{0.5}$) gel prepared by a method, entry 7 upon temperature change. The water content was determined after storing the gel in a chamber at each temperature for 30 min.

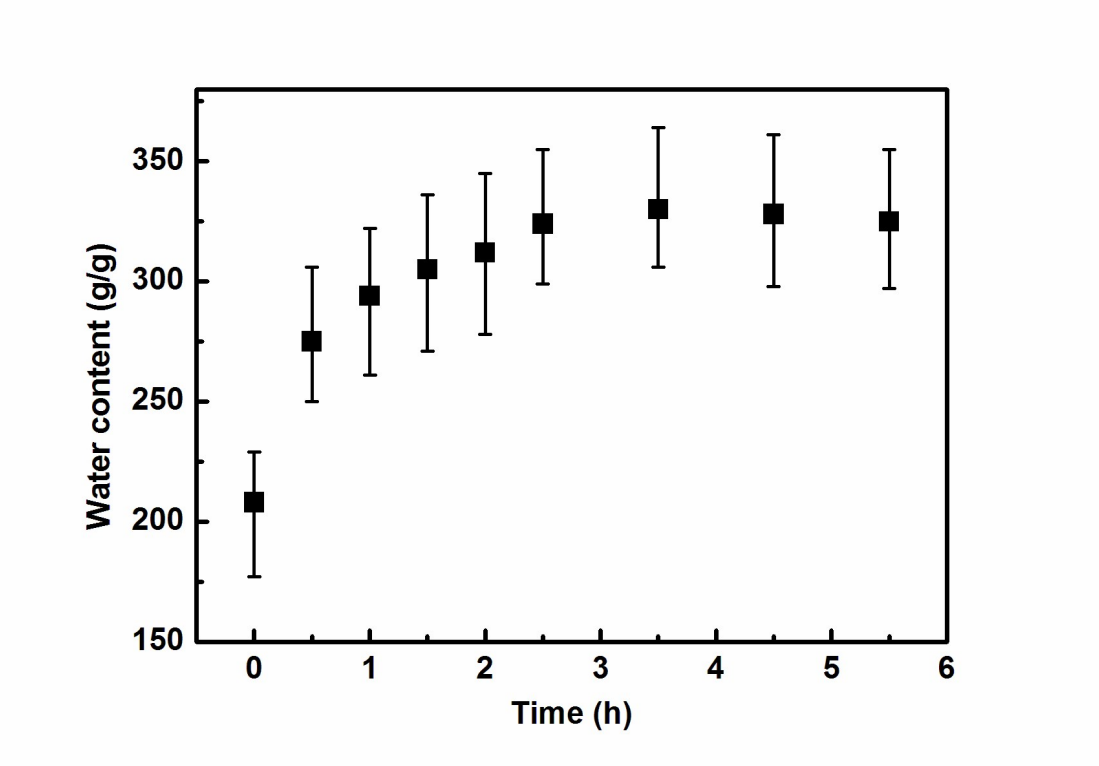

Fig. S9 Time-dependent water content (g/g) of poly([P_{4446}][MC3S]$_{0.5}$-*co*-[P_{4448}][MC3S]$_{0.5}$) gel prepared by a method, entry **7** at 5 °C after desorption of water *via* the LCST behaviour.