Supporting Information

Preparation of ionized polyrotaxane cross-linker (iPR-C)

(Detailed results were shown in the supporting information for our previous paper: Imran, A.B., Esaki, K., Gotoh, H., Seki, T., Ito, K., Sakai, Y., Takeoka, Y., "Extremely stretchable thermosensitive hydrogels prepared by introducing polyrotaxane-based slide-ring cross-linkers and ionic groups into the polymer network"

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METHODS

Materials

PRs with different molecular weights were purchased from Advanced Soft Materials (Kashiwa, Japan) and were used without further purification. NIPA was purified by recrystallization from toluene/n-hexane. Succinic anhydride (Tokyo, Kasei, Japan), carbonyl diimidazole (Kanto Chemical, Japan), dimethyl sulfoxide (Kanto Chemical), isopropyl alcohol (Kishida Chemical, Japan) dibutyltin dilaurate (DBTDL; Tokyo Kasei Kogyo, Tokyo, Japan) and butyl hydroxyl toluene (BHT; Tokyo Kasei Kogyo) were purchased as reagent-grade materials and used as received. 2-acryloyloxyethyl isocyanate (Showa Denko K.K., Japan) was used as received. Milli-Q ultra-pure water was used in all experiments. Dialysis membranes with a molecular weight cut-off of 1,000 were purchased from Spectrum Laboratories, Inc.

Preparation of ionic polyrotaxane (iPR)

Here, we explain the typical synthesis of iPR using PR20 as a starting compound. Carbonyl diimidazole (0.90 g) dissolved in dry DMSO was slowly delivered into a PR20 (2.0 g) solution prepared using dry DMSO (approximately 10 ml) under a nitrogen atmosphere. The solution was stirred for 16 hours at 40 °C. Following this step, succinic anhydride (2.25 g) dissolved in dry DMSO (10 ml) was funnelled into the solution, which was stirred for an additional 7 hours. After the reaction, the product was purified by dialysis treatment using DMSO and water, and freeze-dried. The number of modified carboxyl groups in the PR was estimated by ^{1}H-NMR.

Preparation of ionized polyrotaxane cross-linker (iPR-C)

The preparation of the ionized polyrotaxane cross-linker (iPR-C) composed of the ionized PR cross-linker followed a previously reported procedure. In a typical procedure, iPR20 (1.5 g) prepared from PR20, the DBTDL catalyst (3 drops) and BHT (polymerization inhibitor, 3.0 mg) were dissolved in 90 ml of anhydrous DMSO. 2-Acryloyloxyethyl isocyanate (0.22 g) was dissolved in 10 ml of anhydrous DMSO, and the solution was added dropwise to the mixtures with

vigorous stirring in the absence of light. The mixtures were then continuously stirred overnight at 40 °C to ensure that the reactions were completed. iPR20-C was reversed by dialysis using DMSO and water, and the precipitated product was refrigerated. The total number of vinyl groups per iPR was estimated from ^{1}H-NMR spectra. iPR35-C and iPR100-C were also prepared using the same procedure from PR35 and PR100, respectively. The yields of iPR-Cs started from corresponding PRs are more than 80 %.

Temperature dependence of the degree of swelling D/D_0 for NIPA-iPR35-C hydrogels containing 1 wt% of iPR35-C in different aqueous buffer solutions.

The swelling behaviour of the NIPA–iPR-C hydrogels shows little dependence on the solvent pH when the amount of iPR-C is lower than 3 wt%. Although the carboxyl groups of iPR-C can also dissociate in water in response to changes in the pH, the dissociated ion does not affect the transition temperature significantly because the amount of iPR-C is very small and the ionic groups are localised only on the iPR-C cross-linker. Thus, the pH dependence of the temperature response is successfully regulated by controlling the spatial distribution of the ionic groups in the hydrogels via simple chemical modifications of the PR.

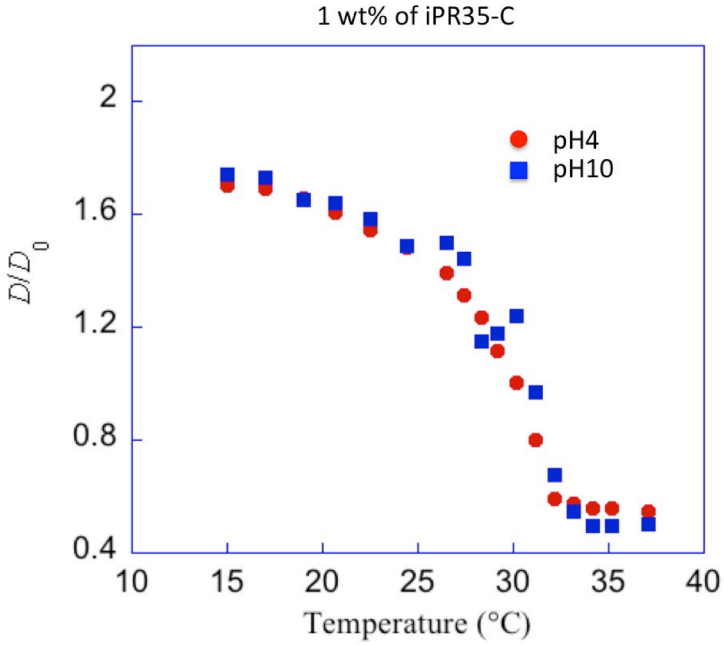

Fig. S1 NIPA-iPR35-C hydrogel with 1.0 wt% of iPR35-C in aqueous solutions with different pHs as a function of temperature. D and D_0 denote the gel diameters at equilibrium and upon synthesis, respectively.