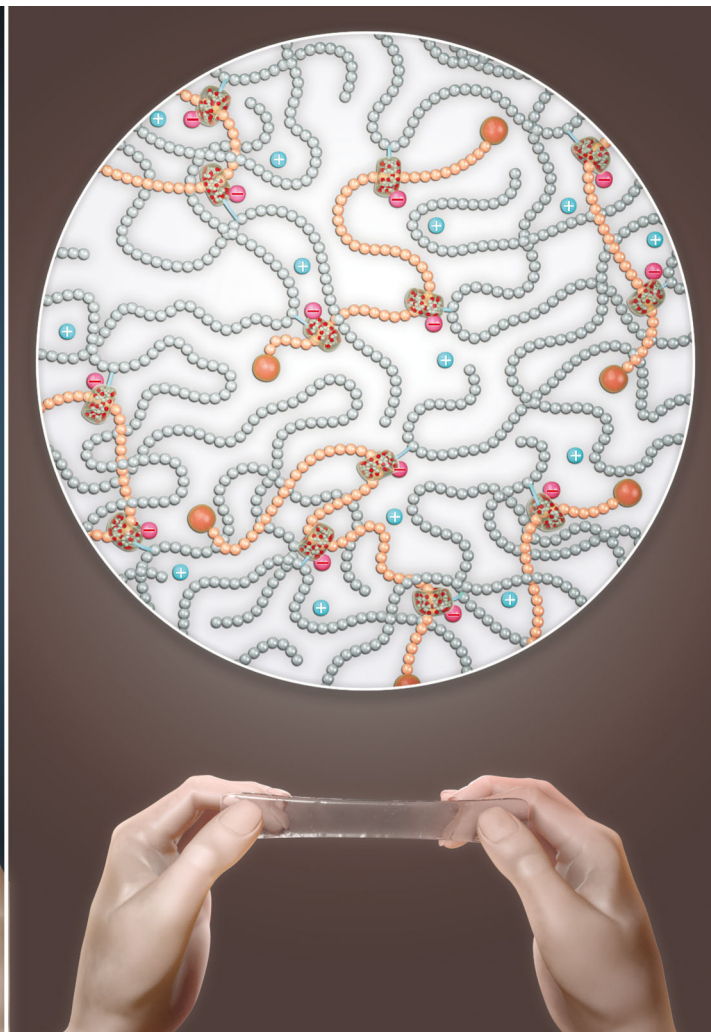
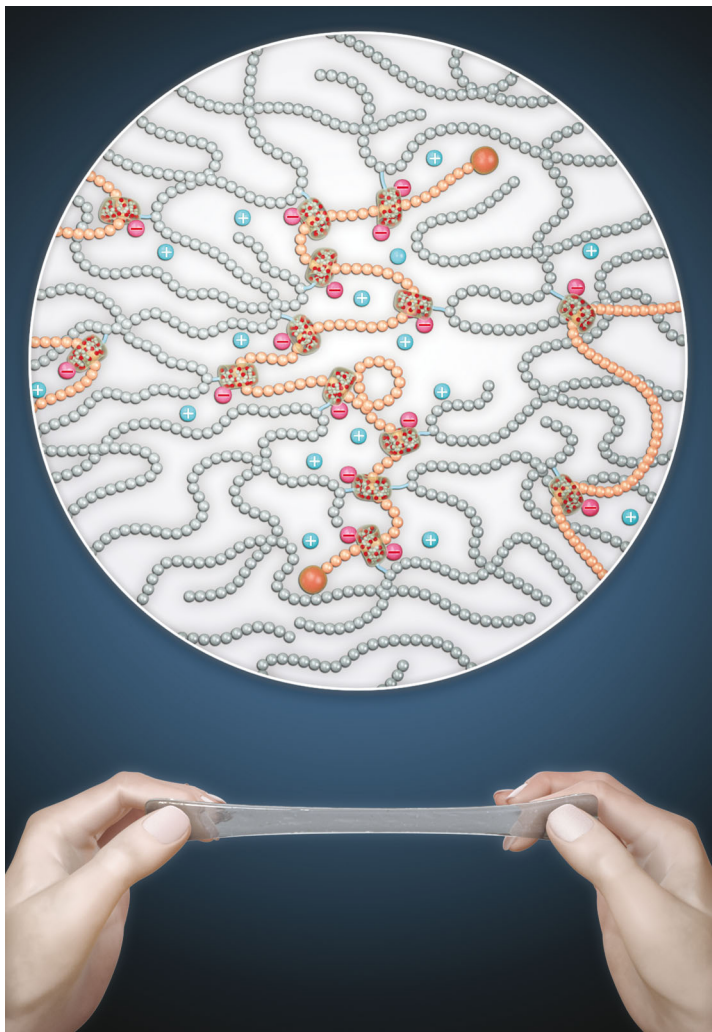




Showcasing work that mainly took place in the Department of Molecular Design & Engineering, Nagoya University, Japan.

Molecular weight dependency of polyrotaxane-cross-linked polymer gel extensibility

This work investigates the influence of the molecular weight of polyrotaxane cross-linkers on the extensibility of polymer gels. We found that the extensibility and rupture strength of the polymer gels are substantially increased with increasing molecular weight of the polyrotaxane cross-linker.

As featured in:



See Yukikazu Takeoka et al.,
Chem. Commun., 2016, **52**, 13757.



Cite this: *Chem. Commun.*, 2016, 52, 13757

Received 20th September 2016,
Accepted 17th October 2016

DOI: 10.1039/c6cc07641f

www.rsc.org/chemcomm

Molecular weight dependency of polyrotaxane-cross-linked polymer gel extensibility†

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This work investigates the influence of the molecular weight of polyrotaxane (PR) cross-linkers on the extensibility of polymer gels. The polymer gels, which were prepared using PR cross-linkers of three different molecular weights but the same number of cross-linking points per unit volume of gel, have almost the same Young's modulus. By contrast, the extensibility and rupture strength of the polymer gels are substantially increased with increasing molecular weight of the PR cross-linker.

A polymer gel is a form of soft material in which a three-dimensionally cross-linked polymer network is swollen with a large amount of solvent. Various types of polymer gels are used in basic research and in practical applications. Polymer gels can be easily prepared by a simple series of steps, such as mixing the necessary compounds with a solvent, degassing the solution, and polymerizing the compounds. They are employed in a wide range of fields because they exhibit functional properties, including super-absorbency, the molecular sieving effect, and slow release of solutes.¹

Stimuli-sensitive polymer gels are composed of covalently cross-linked polymer networks swollen with solvents; they undergo reversible changes in surface² and volume properties^{3,4} in response to environmental changes and applied stimuli. Over the past three decades, these polymer gels have attracted attention from many researchers in various fields because of the potential for new basic properties and applications.⁵ However, most traditional chemically cross-linked polymer gels, including stimuli-sensitive polymer gels, are inherently brittle due to their chemically fixed, inhomogeneous polymer network structure.^{6,7} In the case

of chemically cross-linked polymer gels, stress applied to the polymer networks is concentrated exclusively in the shorter sub-chains between the cross-points in the polymer networks. As a result, the polymer network is easily mechanically disrupted. Recently, many research groups have made various attempts to improve the mechanical properties of polymer gels.^{8–10} However, cumbersome procedures are generally required to obtain such robust polymer gels. A simple and conventional method of preparing mechanically improved stimuli-sensitive polymer gels could facilitate active research on these materials.

We previously reported that a polyrotaxane (PR) composed of cyclic molecules and a linear polymer could be used as a cross-linker to prepare thermo-sensitive polymer gels.^{11–14} The resulting polymer gels exhibit high extensibility and fracture toughness. The PR used contains α -cyclodextrins (α -CDs) as cyclic molecules and polyethylene glycol (PEG) as a linear polymer.¹⁵ Because the inclusion complex composed of α -CD and PEG produces a white precipitate by the simple mixing of these molecules dissolved in water, a stable PR can be obtained by capping the two terminal sites of the inclusion complex using two bulky reactive molecules. This PR is slightly soluble in water and many organic solvents. The properties of the PR can be controlled by modification at the hydroxyl groups of α -CD sites. When modified with appropriate molecules, for example, the PR becomes soluble in water and certain organic solvents.¹⁶ Furthermore, if the α -CDs in the PR are modified with polymerizable vinyl molecules, the PR derivative can become a cross-linker that is useful for preparing polymer gels.¹¹ If such a PR cross-linker is made commercially available, the recipe to prepare polymer gels using the PR cross-linker would be as straightforward as that of conventional polymer gels. When an external force distorts the shape of the polymer gel prepared with the PR cross-linker, the stress concentrated on a portion of the polymer network can be relieved by the sliding motion of α -CDs through a PEG chain in the PR. In the case of conventional polymer gels, the chain length between two cross-points controls the mechanical properties of the polymer gels, such as Young's modulus and fracture strength.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6cc07641f

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In addition to the cross-linking density, the mobility of α -CDs through the PEG chain also affects the mechanical properties of the polymer gels prepared with the PR cross-linker. Comparing the mechanical properties of the covalently cross-linked polymer gel prepared with a traditional cross-linker and the polymer gel prepared with the PR cross-linker, the latter exhibits a lower Young's modulus and higher extensibility due to the mobility of the cross-link points.

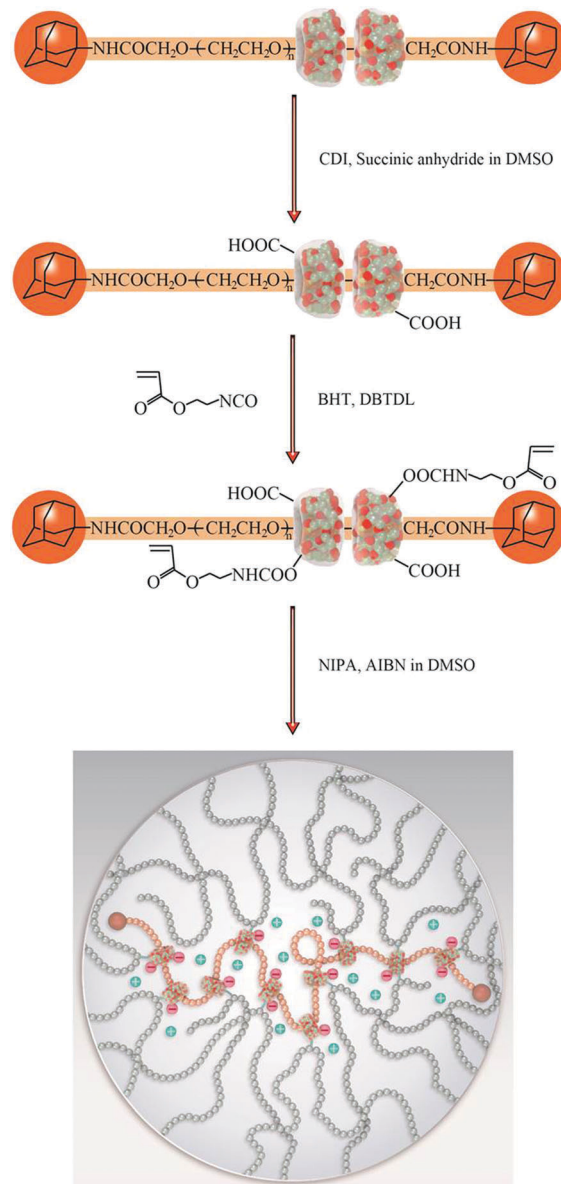
Therefore, it is expected that the range of movement of α -CDs through a PEG chain increases with increasing average molecular weight of the PEG, assuming that the inclusion ratio of α -CDs is constant for PEG with different molecular weights. If such a PR cross-linker with a higher molecular weight of PEG is employed, the resultant polymer gel may exhibit higher extensibility due to the increase in the radius of gyration and the stretchable state of the PR cross-linker, in addition to the increase in the range of movement of α -CD through the PEG chain. This study investigates the effect of the molecular weight of the PR cross-linker on the extensibility of the polymer gel using three different molecular weights of PR; the PR prepared using PEG with molecular weights of 20 000, 35 000 and 100 000 is designated as PR20, PR35 and PR100, respectively.

Harada *et al.* were the first to report a PR composed of α -CD and PEG.¹⁷ However, the major targets of the PR were synthesized with oligomer PEGs, whose molecular weights are lower than 10 000. When using oligomer PEGs, the inclusion ratio of α -CDs against PEG is nearly 100%, where one molecule of α -CD folds two units of an ethylene glycol repeating unit. As the molecular weight of the PEG increases, the inclusion ratio of the ethylene glycol repeating unit in α -CDs becomes smaller.¹⁷ Indeed, the inclusion ratios for PR20, PR35 and PR100 are 28%, 26% and 19%, respectively, *i.e.*, the inclusion ratio decreases with increasing molecular weight of PEG. This inverse relationship is thought to be due to early sediment formation of the PR for larger molecular weights of PEG in water.

A PR with a smaller inclusion ratio is expected to have an increased range of sliding motion for α -CDs through PEG. In addition to the increase in the radius of gyration and the stretchable state of the PR cross-linker incorporated in the polymer network due to the increase in the molecular weight of PEG, the decrease in the inclusion ratio also contributes to the increase in the range of movement of α -CD in the network.

In this study, an ionized PR (iPR) modified with approximately 1.5 carboxylic acid groups per α -CD, which can be soluble in water, was used to prepare the PR cross-linker. The iPR was modified with an average of 1–2 vinyl groups per α -CD, thus forming the cross-linker: iPR-C (Scheme 1).¹⁴ The abbreviated expressions for the iPR-C prepared from PEG with molecular weights of 20 000, 35 000 and 100 000 are iPR20-C, iPR35-C and iPR100-C, respectively.

N-Isopropylacrylamide (NIPA), azobisisobutyronitrile (AIBN) and dimethyl sulfoxide (DMSO) were used as the monomer, initiator and solvent, respectively, to prepare polymer gels using these three different cross-linkers. In a typical experiment, a pre-gel solution consisting of NIPA (224 mg) and each cross-linker (approximately 10 mg) dissolved in DMSO (1.1 g) was maintained at 40 °C over 1 d. The weight percentage of the cross-linkers in the



Scheme 1 Preparation of iPR-C and PNIPA gel using iPR-C.

pre-gel solution is only 0.75. After that, nitrogen gas was injected for 30 min to remove dissolved oxygen from the pre-gel solution. After the addition of AIBN (1.3 mg), the pre-gel solution was transformed into a polymer gel at 60 °C in a glass cell with 1 mm thickness.

The hydrogels, in which DMSO is replaced by water, undergo a reversible change in volume. When heated in water above 32 °C, the hydrogels change from the swollen state to the collapsed state.¹⁸ The swelling ratio of the chemically cross-linked hydrogels swollen with a solvent is known to depend on the number of cross-points per unit volume of the hydrogels.¹⁹ The total number of vinyl sites from each iPR-C dissolved in the pre-gel solution is approximately 6×10^{18} and is approximately conserved across all pre-gel solutions. As a result, the polymer gels obtained in this condition exhibit a similar swelling ratio when swollen with water below 32 °C (Fig. 1). Thus, it is

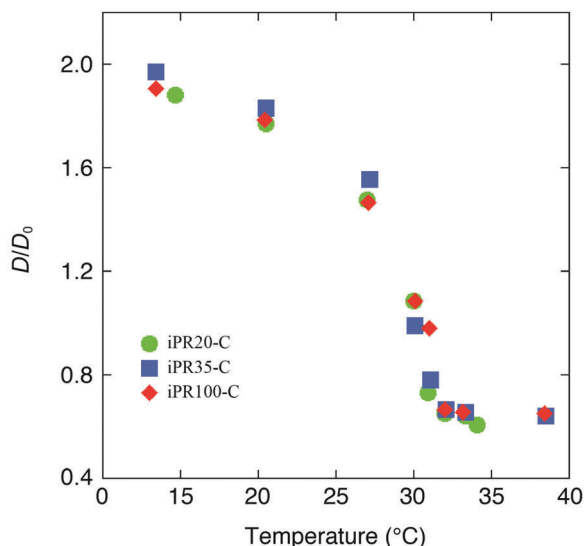


Fig. 1 Swelling behaviours of PNIPA gels prepared using iPR-Cs with different molecular weights as a function of temperature in water. D and D_0 are the diameters of the gel in the equilibrium state at a certain temperature and in the preparative state, respectively. Therefore, D/D_0 is defined as the equilibrium linear swelling degree of the gel.

confirmed that the swelling ratio of the polymer gel prepared with iPR-C is also influenced by the number of cross-points per unit volume of the polymer gel.

The mechanical behaviour of the polymer gels is compared in the as-prepared states. The sample used to measure the stress-strain behaviour of the polymer gels is a strip specimen of 1 mm thickness and 4 mm width. The measurements are started when the length of the polymer gels is 10 mm. The samples are stretched at a speed of 0.5 mm min^{-1} at 25°C to observe the stress and strain behaviour (see ESI,† movies). We

previously reported that the Young's modulus of PNIPA gels prepared with iPR35-C increases with increasing iPR35-C content. The increase in Young's modulus of the polymer gels can be attributed to the increase in the number of cross-points per unit volume of the polymer gels. In this study, we found that the strain and rupture strength of the polymer gel prepared with the same amount of reactive vinyl sites of iPR-C per unit volume are dramatically increased with the increase in molecular weight of the PR cross-linker, whereas the Young's modulus, which is estimated by the initial gradient of the stress-strain curve, remains the same (Fig. 2). The pulley effect occurring at larger deformation is enhanced by the decrease in the inclusion ratio of PEG by α -CD molecules for iPR-C and the increase in the molecular weight of PEG.^{20,21} As a result, the strain and rupture strength of the polymer gel are increased with increasing molecular weight of iPR-C (Fig. 2).

In summary, we investigated the effect of molecular weight of the PR cross-linker on the strain and rupture strength of the polymer gels. It was found that the strain and rupture strength of the polymer gel are increased with increasing molecular weight of the PR cross-linker. As expected, we can say that with increasing molecular weight of PEG the effective range to move CDs along with PEG chain increases under external force. As a result, the strain and rupture strength of the polymer gel are enhanced with the increase in the molecular weight of iPR-C. Because the PR cross-linker can react with the many types of reactive vinyl monomers, various types of polymer gels with favourable mechanical performance can be prepared using this cross-linker.

Y. T. and K. I. acknowledge the support of IMPACT for the project "Realizing an Ultra-Thin and Flexible Tough Polymer". *N*-isopropylacrylamide was kindly provided by Kohjin (Tokyo, Japan). All PRs were kindly provided by Advanced Soft Materials (Kashiwa, Japan).

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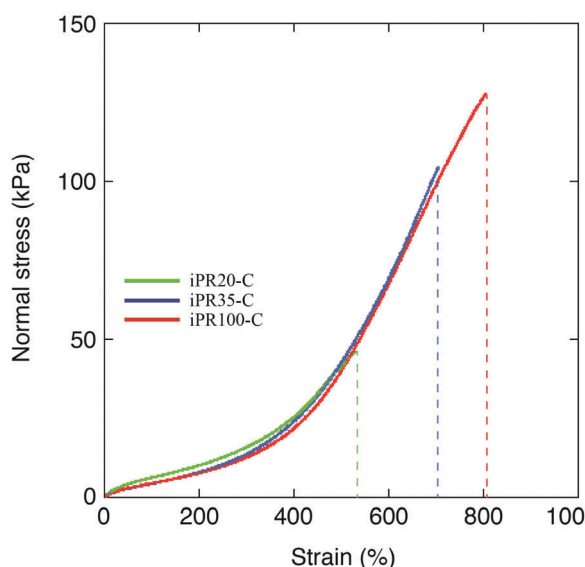


Fig. 2 Stress-strain curves of as-prepared PNIPA gels prepared using iPR-Cs with different molecular weights.