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Strain Hardening and Highly Resilient Hydrogels Crosslinked by Chain-Extended Reactive Pseudo-Polyrotaxane

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Cite this: DOI: 10.1039/xoxxoooooox

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

www.rsc.org/

Strain hardening and high resilience are two unique mechanical characters of many soft biological hydrogels. However, these properties, especially the strain hardening behaviour, are generally not seen in synthetic polymer hydrogels. Herein, hydrogels are prepared by free radical copolymerization of acrylamide and chain-extended vinyl modified pseudo-polyrotaxane, which acts as multifunctional cross-linkers. The reactive pseudo-polyrotaxane is based on β-cyclodextrin monomer and amine terminated PEG-PPG-PEG (Pluronic F127). The obtained hydrogels can be stretched 10 to more than 26 times their original length before breaking, withstand compression strain of 95% and even 98% without fracture. Stretching tensile tests show obviously strain hardening behaviours at large stretching and compression deformation regime. The strain hardening behaviour in stretching deformation is considered to be the orientation and aggregation of the moveable cross-linkers along the axial polymer backbone. And the formation of a second supramolecular network due to the chain-extension effect may also be responsible for it. Highly resilient behaviours with almost no hysteresis and residual strains are also observed even with a maximum strain of λ = 12 because of the inherent freely moveable character of the cross-linkers.

Introduction

The fast growing area of hydrogels is of utmost importance for fields such as artificial implants, biomedical devices, tissue engineering and regenerative medicine, etc., due to their unique properties such as similar flexibility, high water content, and molecule diffusion to natural soft tissues.[1-5] Thus, during the past years, various functional hydrogels including stimuli responsive gels, self-healing gels, shape-memory gels and so on were developed for different bioapplications.[6-11] While, classical hydrogels are often mechanically weak and brittle, just like jelly or paste. It is these disadvantages that severely limit their great potential applications as ideal structural biomaterials, where mechanical performance is required. Therefore, from the beginning of this century, several kinds of hydrogels, such as sliding gels,[12] nanocomposite gels,[13] double-network gels,[14] macromolecular microsphere composite gels,[15] tetra-PEG based gels,[16] and our polyurethane-urea supramolecular (PUUS) hydrogels,[10,11,17] were developed to match the mechanical requirements.

However, there are still many other special mechanical characters of biological hydrogels deserve material scientist's attention. For example, many kinds of biological proteins/polymers based hydrogels demonstrate unique viscoelastic properties differing from synthetic polymer hydrogels. These unique viscoelasticity of biopolymers based hydrogels is fundamental to their biological function and the maintenance of normal physiology. For instance, actin, collagen, fibrin, vimentin, neurofilament etc. based hydrogels show strain hardening behaviour-a sharply increase in material stiffness at large strains, thereby preventing large deformations that could threaten tissue integrity.[18-20] Meanwhile, elastin and resilin based biological hydrogels can be reversibly deformed without energy loss. These hydrogels are also well-known as having resilience-an important feature developed by nature storage that facilitates repeated movement.[21-23] But these protein based human made hydrogels usually do not show high ductility, which significantly limits the scope of their potential biomedical applications.

And so, synthetic hydrogels with similar viscoelastic properties of biological soft tissues/hydrogels are of high importance and interest to the fundamental, design and application of nowadays hydrogel based biomaterials and many other soft materials, such as thermo plastic elastomers. Highly resilient behaviour was recently observed in several synthetic hydrogels systems.[24,25-28] While, strain hardening was mainly observed in protein/biopolymer based hydrogels,[18-20,29,30] and was recently observed in the nanocomposite gels for the first time. Although, strain hardening behaviour have been widely observed in the compressing deformation condition,[14-17,31,32] synthetic hydrogels with both strain hardening and high resilience

behaviours in both stretching and compression process have been rarely reported because this may require complicated chemical synthesis and rational molecular design.

As one of the famous mechanically strong hydrogels, sliding gels have been widely studied due to their unique topological characteristics and various potential applications.[12,33] However, traditional sliding hydrogels are always prepared by crosslinking of polyrotaxane (PR) based on PEG and α-cyclodextrin (α-CD) via complicate procedures. To obtain pure PR, excessive α-CD has to be completely removed before crosslinking to avoid non-effective crosslinking between free α-CD and the used crosslinking reagent, and this often yields low conversion of PR. At the same time, the crosslinking reaction often can only be conducted in a very limited number of solvents due to the poor solubility of the formed PR. And thus, hydrogels can only be obtained after water exchanging process to remove the organic solvents/inorganic compounds. On the other hand, pseudo-polyrotaxane (PPR) and PR based on PPG or PEG-PPG-PEG triblock copolymers and β-cyclodextrin (β-CD) have been studied long time ago.[34-38] However, to our knowledge, sliding gels using β-CD as the moving crosslinkers are still not yet reported. This may mainly because of the difficulty in preparation of β-CD based PR due to its so large cavity that it is difficult to find suitable stopper groups.[37]

In this work, we present a novel kind of synthetic sliding hydrogel based on β-CD and PPR via a simple modular method. The hydrogels are fabricated by UV initiated free radical copolymerization of acrylamide and vinyl modified PPR constructed by β-CD monomer and amine terminated PEG-PPG-PEG triblock copolymer (Scheme 1). Particularly, the hydrogels not only show good ductility, but also have excellent strain hardening and high resilient property.

Experimental section

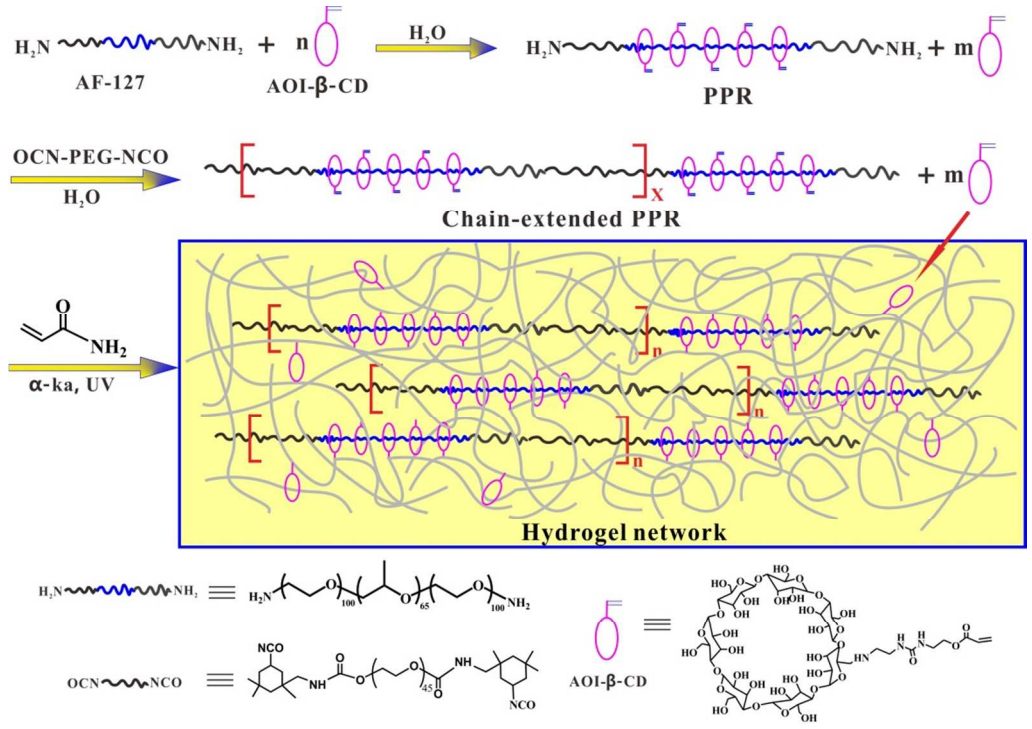
Materials

Pluronic F-127 (PEG-PPG-PEG) was obtained from Sigma-Aldrich. Polyethylene glycol (PEG, Sinopharm Chemical Reagent Co., Lcd) with average M_n = 2000 g/mol were dried at 80 ºC under vacuum in presence of P_2O_5 overnight before use. β-Cyclodextrin (β-CD), N,N-carbonyldiimidazole (CDI), ethylenediamine and acrylamide were purchased from Sinopharm Chemical Reagent Co. Ltd. The photo-initiator α-ketoglutaric acid (α-ka, 99%) was purchased from Fluka. Isophorone diisocyanate (IPDI) was purchased from Aladdin. 2-isocyanatoethyl acrylate (AOI) was kindly donated by Showa Denko Company. The catalyst dibutyltin dilaurate (DBTDL) was purchased from TCI. N,N-Dimethylformamide (DMF) and tetrahydrofuran (THF) was dried by 4Å molecular sieves before use.

Synthesis

Details of the synthesis of H_2N-PEG-PPG-PEG-NH_2 (AF-127), AOI-β-CD and OCN-PEG-NCO can be found in supporting information (ESI).

Hydrogel preparation



Scheme 1. Synthetic procedure of the hydrogels prepared by free radical copolymerization.

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As shown in Scheme 1, the hydrogels were prepared by UV irradiated free radical copolymerization of acrylamide and chain-extended vinyl modified PPR, which acts as multifunctional supramolecular cross-linkers. Here, the PPR is based on AOI-β-CD monomer and amino terminated Pluronic F127 (AF-127). A typical synthetic procedure of the hydrogel is as follows. Firstly, AOI-β-CD was added into the aqueous solution of AF-127 (0.5, 1.0 or 2.5 wt. %), and the molar ratio of AOI-β-CD to AF-127 was 5:1, 10:1, or 15:1. The mixture was then stirred for 2 days at room temperature to let AOI-β-CD fully thread onto the PPG chains. Secondly, isocyanate end capped PEG (OCN-PEG-NCO) was added into the solution to yield chain extended PPR due to the quick reaction between -NH_2 and -NCO. Finally, acrylamide and α-ka (photo initiator) were added into the chain extended PPR solution, and the mixed solutions were then transferred into transparent plastic syringes and sealed. The sealed plastic tubes were irradiated by 365 nm UV light (40 W, the distance between the samples and the lamp was 10 cm) for 1 h. For all the samples, the concentrations of acrylamide and α-ka were fixed at 10.0 wt. % and 0.2 wt. %, respectively. The obtained hydrogels are named as x%-yCD, where x and y denoted the weight concentration of AF-127 and the molar ratio of AOI-β-CD to AF-127. For example, 1.0%-10CD means the concentration of AF-127 is 1.0 wt. % and the molar ratio of AOI-β-CD to AF-127 is 10.

Characterizations

^{1}H NMR spectra in D_2O were recorded using a 400 MHz Inova NMR spectrometer. Rheology measurements were performed on a HAAKE Rheometer (RS 6000) with a parallel plate accessory (20 mm in diameter). The existence and extent of the linear viscoelastic regime were determined by measuring the dynamic shear storage modulus (G') and loss modulus (G"), as a function of strain ($0.001< \gamma < 10$) at an angular frequency of 6.28 rad/s. All the measurements were carried out within the linear viscoelastic range, where G' and G" are independent of strain. Tensile and compression tests were carried out on a universal tensile test machine (KJ-1065B, Kejian-tech) with a 50 N loading cell; the cross-head speed of the tensile and compression measurements was 50 mm/min and 3 mm/min, respectively. The normal force F and the gap l (for tensile test) or h (for compression test) between the two clamps or plates were recorded. The true stress σ_{true} was adopted as previous report.[31] The nominal stress $\sigma_{nominal}$ was estimated as $\sigma_{nominal} = F/S_0$, S_0 is the original cross-section area of the gel before deformation, $\sigma_{true} = \sigma_{nominal} \times l/l_0$ or $\sigma_{true} = \sigma_{nominal} \times h/h_0$ (in the compression case). Morphological study of the cross-section of the freeze-dried hydrogel sample was carried out on a Hitachi S-4700 scanning electron microscope (SEM). Sample for SEM was sputter coated with a thin layer of Au prior to the observations to prevent samples charging problems.

Results and discussion

As shown in Scheme 1, the hydrogels were prepared by simple free radical copolymerization of acrylamide and chain-extended vinyl modified PPR under UV irradiation. Here, α-ka (α-Ketoglutaric acid) was used as the photoinitiator. AF-127 was synthesized from Pluronic F127 according to previous reports.[35] Details of the synthesis of AOI-β-CD and isocyanate terminated PEG (OCN-PEG-NCO) were given in ESI. For all the hydrogel samples, the concentration of acrylamide was fixed at 10.0 wt. %. The obtained hydrogels were named as x%-yCD, where x and y denote the weight concentration of AF-127 and the molar ratio of AOI-β-CD to AF-127. For example, 1.0%-10CD means the used concentration of AF-127 is 1.0 wt. % and the molar ratio of AOI-β-CD to AF-127 is 10. Of special note, the present strategy is totally different from Takeoka's novel sliding gels, which was prepared by copolymerization of N-isopropylacrylamide and adamantane end capped vinyl modified PEG/α-CD based ***PR*** in ***DMSO***.[39] And compared with traditional and Takeoka's novel sliding gels, the advantages of the present method as shown in Scheme 1 include: 1) the whole procedure was carried out in one pot with three steps using water as solvent; 2) instead of attachment of bulky end group yielding low conversion of PR, chain-extension was used to get long chain multiblock PPR (chain-extended PPR) so that there were still enough threaded AOI-β-CD monomers on the polymer main chain in the gelation process; 3) there was no need to remove the free AOI-β-CD monomers in the first two steps, because they can copolymerize with acrylamide in the last step without yielding crosslinking points. SEM micrograph showing the cross section of the freeze-dried 1.0%-15CD hydrogel sample can be found in Fig S2 in ESI.

Rheology experiments (Fig 1 and Fig S3 in ESI) show that the storage modulus (G') at 10 rad/s of the resulting hydrogel range from 500 Pa to 1000 Pa, these are comparable to the traditional sliding hydrogels (500~2000 Pa).[12] At the same time, G' depends both on the concentration of AF-127 and the molar ratio of AOI-β-CD to AF-127. As shown in Fig 1a and Fig S3a-b in ESI), at a fixed concentration of AF-127, G' increases with increasing concentration of AOI-β-CD. Similar trends are also observed with increasing concentration of AF-127 at fixed molar ratio of AOI-β-CD to AF-127 (Fig 1b and Fig S3c-d in ESI). This is all because of the increased cross-linking density of the obtained hydrogels with increasing concentration of AOI-β-CD (Fig 1a) or AF-127 (Fig 1b).

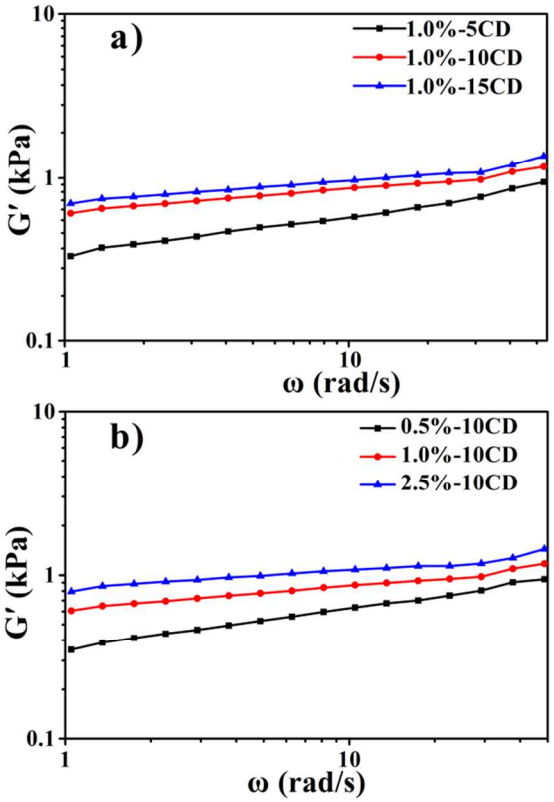

Fig 1. Shear storage modulus of the obtained hydrogels. a) the concentration of AF-127 is fixed at 1.0 wt. %, and the molar ratios of AOI-β-CD to AF-127 are 5, 10 and 15; b) the molar ratio of AOI-β-CD to AF-127 is 10, and the concentrations of AF-127 are 0.5, 1.0 and 2.5 wt. %. For all the samples, the concentration of acrylamide is 10 wt. %.

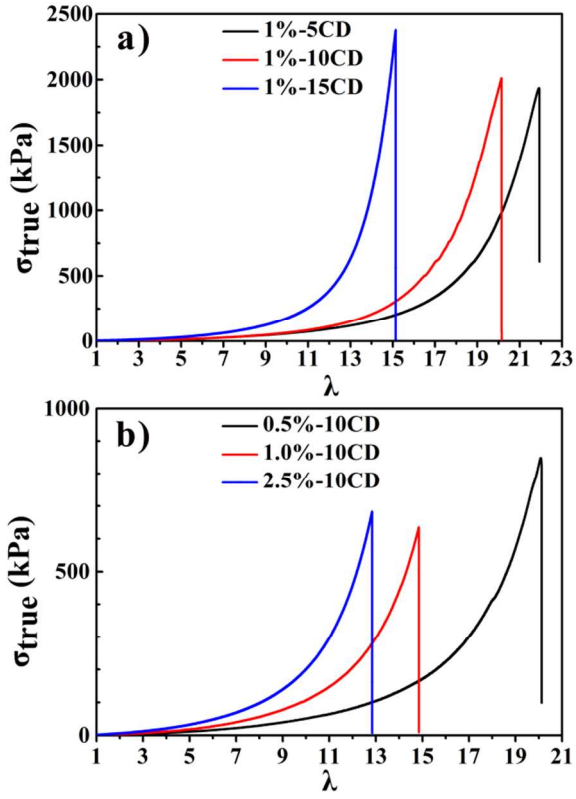

Fig 2. Stretching tensile test curves of the obtained hydrogels as shown in Fig 1. $\lambda = l/l_0$, l and l_0 are the stretched and original length of the sample.

Tensile tests were carried out to further investigate the viscoelastic property of the resulting hydrogels. The elongation ratio λ is taken as the deformed length l related to the original length l_0, $\lambda = l/l_0$, the true stress is adopted as $\sigma_{true} = \sigma_{norminal} \times l/l_0$ according to previous report.[31] As shown in Fig 2 and Fig S4 in ESI, the hydrogels show excellent ductility and can be stretched 9 to more than 26 times their original length before breaking. At the same time, at a fixed concentration of AF-127 (Fig 2a and Fig S4a-b), σ_{true} increases with increasing concentration of AOI-β-CD, while λ at breaking decreases. Similar trends are also observed with increasing concentration of AF-127 at fixed molar ratio of AOI-β-CD to AF-127 (Fig 2b and Fig S4c-d in ESI). This is all because of the increased cross-linking density of the obtained hydrogels with increasing concentration of AOI-β-CD or AF-127, and also in accordance with the results in Fig 1. The network's strength increases with increasing crosslinking density, but its extendibility will decrease.[25,28]

Intriguingly, obvious strain-hardening behaviour-a sharply increase in stress at large strain regime is observed in Fig 2 and Fig S4 in ESI. For example, in the case of sample 1%-15CD (blue curve in Fig.2a), σ_{true} slowly and almost linearly increased to 120 kPa in a large strain region from λ = 1 to 9, while, it abruptly increases to 2400 kPa at λ = 15, which is 20 times that at λ = 9. Furthermore, as the results shown in Fig 2 and Fig S4 in ESI, the degree of the strain-hardening phenomena also depends both on the concentration of AF-127 and the molar ratio of AOI-β-CD to AF-127. Although the underlying mechanism is still not fully understood, possible mechanism of the strain-hardening behaviour may be due to: 1) similar to classic sliding gels,[40] the sliding cross-linkers (β-CD) can orientate along the PPG chains and form aggregates while stretching, however, β-CD is more like to locate on the middle PPG blocks due to stronger hydrophobic interactions other than on the PEG chains,[35,36,38] and thus much higher stress is needed for the further sliding of the formed aggregates along the *PEG* chains at larger strain regime. This is different from traditional sliding gels, where the formed aggregated of α-CD cannot be further moved due to the bulky end group leading to breaking of the gels; 2) the formation of a second supramolecular network due to the chain extension effect may also be responsible for it. This is because the chain extension effect not only yields strong hydrogen bonding units (urea) due to the reaction between –NCO and $–NH_2$, but also greatly improves the chain length of the axial polymer backbone. Thus a second weak supramolecular network forms due to the strong hydrogen

bonding interaction between urea groups and the enhanced chain entanglement because of increasing chain length. Just like the function of the second network in the DN gels, the second weak network greatly improves the mechanical property of the resulted hydrogels in large deformation regime.[14] This is different from traditional sliding gels, where the linear polymer backbone only acts as an axis for the sliding of the threaded cyclic molecules. On the other hand, control experiments (Fig S5 in ESI) further show that the chain-extension effect does not have obvious influence on the elongation ratio of the hydrogels, but it greatly improves the strain-hardening property in higher strain regime. Additionally, although, strain hardening behaviour have been observed in the compressing deformation condition of many other hydrogels including sliding hydrogels,[14-17,31,32] to our knowledge, this is the first time that such obvious strain hardening behaviour in *stretching deformation* of sliding hydrogels is observed.

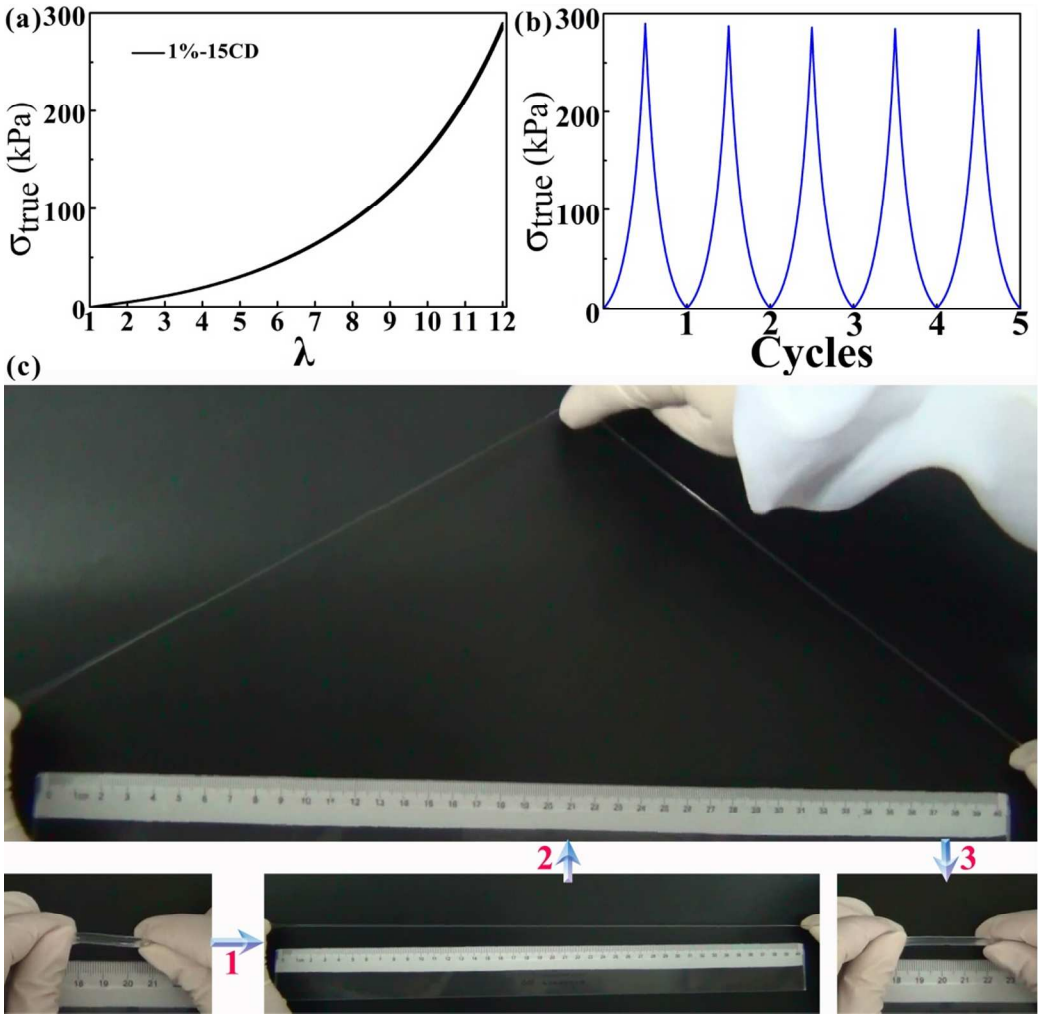

Fig 3. Cyclic tensile test curves (a, b) and photo images (c) of the 1%-15CD sample. $\lambda = l/l_0$, l and l_0 are the stretched and original length of the sample.

Another interesting and important character of the obtained hydrogel is their highly resilient property. For simplicity, sample 1%-15CD with the best strain hardening behaviour is chosen for the cyclic tensile tests. As shown in Fig 3, with a maximum strain of $\lambda = 12$, the 5-cycle loading-unloading curves perfectly overlap with each other and show negligible loops (Fig 3a), indicating that there is almost no hysteresis or permanent network damage in the cycles. It is necessary to notice that there is also almost no decrease of the maximum stress of the immediately followed 4 cycles in comparison with the first cycle (Fig 3b), which further confirms the highly resilient behaviour. Images in Fig 3c (details of can be found in Movie S1 in ESI) show that even after being stretched to about 15 times its original length, the hydrogel still can almost recover to its original shape. The highly resilience should be attributed to the unique pulley effect of the *freely* moveable sliding crosslinks, which makes it different from physical and chemical gels.[33] Note again, although sliding gels have been widely studied previously, to our knowledge, this may be the first cyclic tensile test showing such excellent resilient behaviour.

Besides the excellent stretching property, the hydrogel also shows nice compression behaviour. As shown in Fig 4, the

hydrogel can withstand 95% (sample 1%-15CD) and even 98% (sample 1%-5CD) compression strain without breaking.

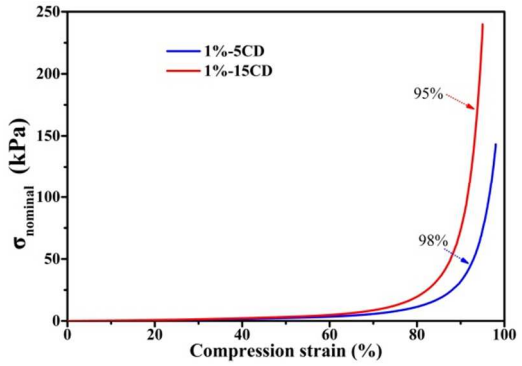

Fig 4. Compression tests curves of sample 1%-15CD and 1%-5CD with a maximum compression strain of 95% (the up limit of the machine, 50 N) and 98% (the minimum gap between the two plates of the machine), respectively, without breaking. $\sigma_{nominal} = F/S_0$, compression strain = $(\Delta h/h_0) \times 100\%$.

Moreover, 5-run cyclic compression test with a maximum compression strain of λ' = 0.1 ($(\Delta h/h_0) \times 100\% = 90\%$) is also conducted. Although, unlike the cyclic tensile tests, hysteresis or energy loss is observed during the loading and unloading compressing process, all immediately subsequent cycles almost follow exactly the same procedure as for the first cycle (Fig 5a). This observation reveals that a full recovery to the initial state is reached during the time scale of the experiment. Additionally, there is also no decrease of the maximum stress in the immediately followed 4 cycles in comparison with the first cycle (Fig 5b). Fig 5c (details of can be found in Movie S2 in ESI) further demonstrates the highly ductile and resilient behaviour of the hydrogel in repeated compression deformation. Additionally, as shown in Fig 5a and Fig S5, the hydrogel also shows clearly strain hardening behaviour in the compression process. This is in accordance with Ito's recent results observed in sliding gels.[32]

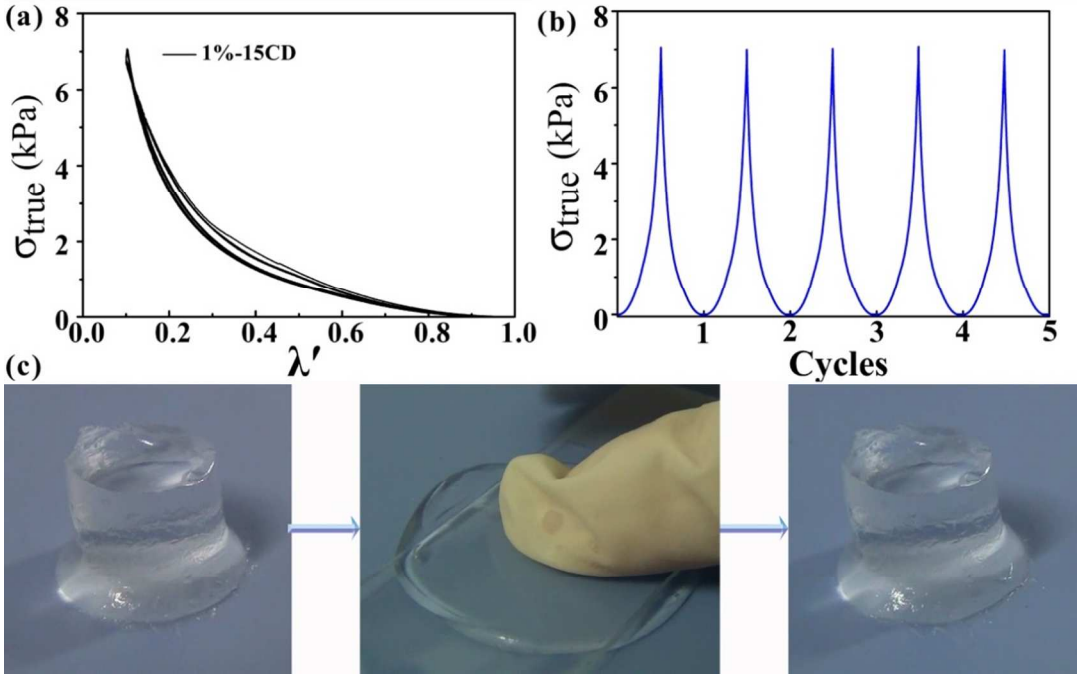

Fig 5. Cyclic compression test curves (a, b) and photo images (c) of the 1%-15CD sample. λ' = h/h_0, h and h_0 are the compressed and original height of the sample.

These highly resilient behaviours demonstrate that there should be almost no permanent damage of the hydrogel's network or dethreading of β-CD during both stretching and compression deformation, which indicate that the long PEG chains can act as an end capping block with similar functions of the bulky end-groups in PR, because β-CD is more like to locate on the PPG chains due to stronger hydrophobic interactions other than on the PEG chains.[35,36,38] And the chain extension effect may further enhances this function due to the formation of strong hydrogen bonding interactions and the increasing chain length and entanglement of the axial polymer backbone.

Conclusions

In summary, hydrogels with obvious strain-hardening and high resilience properties in *both stretching and compressing* process were constructed by simple free radical copolymerization of acrylamide and chain-extended vinyl modified PPR, which acted as multifunctional cross-linkers. Instead of crosslinking of low yielding PR with bulky end group in organic solvents via complicate process, here, with the chain-extension technique the whole procedure can be carried out in one pot in water. Obvious strain hardening behaviour in stretching deformation is observed for the first time, which is considered to be the orientation and aggregation of the moveable cross-linkers along the axial polymer backbone. And the chain-extension induced formation of a second

supramolecular network may also be responsible for this. The freely moveable character of the cross-linkers provides the hydrogels with high resilience properties. These results not only exhibit a new member of ***β-CD*** based sliding-ring soft materials, but also provide progress toward addressing the challenges of using synthetic hydrogels to achieve biological soft tissue/hydrogel's unique viscoelastic properties. The strain hardening and highly resilient characters combined with the simple modular synthetic strategy present appealing avenues for design, fundamental and application studies of new biomimetic materials and other new soft materials with unique bio-mimic viscoelastic behaviours.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (NSFC, no. 21304063 and 21274102) and the Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions.

Notes and references

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Electronic Supplementary Information (ESI) available: Synthesis, Fig S1-5, Movie S1 and S2. See DOI: 10.1039/b000000x/

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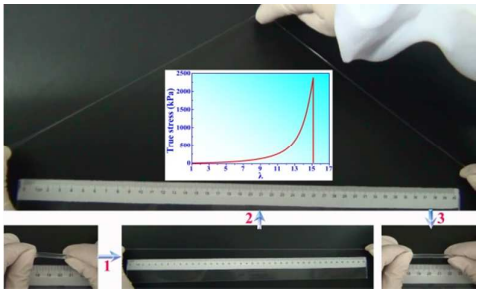

Hydrogels with obvious strain-hardening and high resilience properties in both stretching and compressing process are constructed by simple free-radical copolymerization of acrylamide and reactive Pseudo-Polyrotaxane.