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Enhanced toughness in highly entangled hydrogels *via* non-covalent molecular hooks

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Hydrogels with enhanced toughness have received increasing attention due to their potential for load-bearing applications. Recent findings have demonstrated that highly entangled networks are capable of forming such materials, yet their fabrication generally necessitates a covalent cross-linker, limiting their processability and applicability. In this work, we found that poly(ethylene glycol) methyl ether acrylate (PEGmeAc) can serve as a non-covalent cross-linker for highly entangled poly(acrylamide) networks in dilute state, imparting extreme stretchability (6600%) and toughness (26 MJ m^{-3}) to the hydrogels that otherwise flow within minutes. Oscillatory and rotational rheology demonstrates that the incorporation of 1 mol% of PEGmeAc is sufficient to provide structural stability to the hydrogel, increase relaxation time and improve elastic response, and severely inhibits disentanglement under shear. We hypothesized that this effect was caused by a combination of hydrogen bonding and topological entanglements, making PEGmeAc act as "hooks" within the network. The mechanism was confirmed through a combination of dissolution assays and nuclear Overhauser enhancement spectroscopy (NOESY), which showed that hydrogen bonding and topological entanglements are at play. Consequently, the incorporation of small quantities of such monomers into hydrogels may open new pathways to enhance the mechanical properties of soft materials.

New concepts

We demonstrate an advancement in hydrogel design by introducing *poly(ethylene glycol) methyl ether acrylate* (*PEGmeAc*) as a non-covalent cross-linker that transforms ultra-high molecular weight poly(acrylamide) gels (UHMW pAAm) into extremely stretchable and tough hydrogels. Through this approach and by using only 1–5 mol% PEGmeAc as a comonomer, a hydrogel is formed, which achieves a stretchability of 6600% and a toughness of 26 MJ m^{-3}. This is a significant improvement over pAAm control hydrogels, which flow within minutes. Unlike traditional cross-linking strategies, our method leverages hydrogen bonding and the creation of additional topological entanglements to stabilize the network, avoiding permanent bond chemistry. PEGmeAc acts as a dynamic "hook" within the entangled matrix, resisting flow and disentanglement under stress without sacrificing softness or flexibility. This work introduces a new design principle for tough, highly elastic hydrogels—reinforcing entangled networks *via* reversible, non-covalent interactions. It provides a generalizable, low-additive strategy that could be extended to a variety of hydrogen bond-compatible polymers. As such, the concept opens new pathways in materials science for engineering high-performance soft materials suitable for load-bearing, biomedical, and wearable applications, all while maintaining structural integrity without covalent constraints.

Introduction

The development of hydrogels with increased toughness has surged due to their promising potential for load-bearing applications. To enhance mechanical properties, non-covalent interactions are often introduced, such as hydrogen bonding, ionic interactions, host–guest chemistry, and self-assembling structures, or through the fabrication of (nano)composite materials, among others.[1] Due to the high level of chemical complexity,

such modes of energy dissipation generally require sophisticated molecular design of monomers and cross-linkers. Despite its simplicity and crucial impact on the material's mechanics, the role of entanglements as an energy dissipation mechanism in hydrogels has often been overlooked.

Recently, several studies suggested that highly entangled systems can impart both high toughness and stiffness to materials, without compromising their stretchability.[2–5] In these works, the polymer entanglements greatly outnumbered covalent cross-links within the network, which could be achieved by reducing the amount of initiator and/or covalent cross-linker, favoring the formation of UHMW chains and entanglements, respectively. By reducing the contribution of covalent cross-links to the mechanical properties, the effect of entanglements was fully leveraged and the mechanical stress was efficiently equilibrated through the sliding of polymer chains rather than their fracture.[2,6] The concept of highly

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entangled hydrogels has since been expanded to the fabrication of zinc metal batteries, providing enhanced mechanical stability and increased ion transport for improved cycling stability,[7,8] or for use in additive manufacturing, enabling the 3D printing of high-resolution, multimaterial structures.[9] Furthermore, a recent work by Wang and co-workers integrated a highly entangled network into double network hydrogels to engineer materials with high toughness and fracture energies.[10] Due to the highly percolated nature of the polymer chains, energy storage was primarily based on entropy loss, resulting in extremely low hysteresis upon cyclic tensile testing and thus nearly perfect elastic behavior. In one of our recent works, we studied the effect of the molecular weight of highly entangled polyacrylamide (pAAm) on its gel properties.[11] When ultra-high molecular weights (UHMW) of above M_n = 3 MDa were reached, highly entangled hydrogels were obtained under dilute conditions (14 wt%) even though no covalent cross-linker was present. While the polymer molecular weights were successfully tied to the rheological properties of the hydrogels, fully leveraging the mechanical potential of UHMW chains was not possible due to their ability to flow on longer timescales.

In this work, we solve this problem by introducing small quantities of a short PEG methyl ether acrylate (PEGmeAc) comonomer to form a comb-like architecture, which provides structural stability and critically enhances the mechanical properties of the UHMW hydrogel (Fig. 1a). While it is known

that comb-copolymers can increase viscosity and reduce relaxation times in the melt,[12] and covalent comb-type acrylamide-based hydrogels have been explored for a variety of topics,[13–17] such architectures have never been applied to UHMW polymer hydrogels. In this report, we introduce PEGmeAc as a low-cost additive in small quantities into the UHMW polyacrylamide gels. As a result, the short PEG side chains non-covalently interact as molecular hooks with disparate UHMW chains via a mix of hydrogen bonding and topological entanglements (Fig. 1a). We demonstrate this through mechanical and spectroscopic characterizations. The markedly improved mechanical properties are characterized through uniaxial tensile tests and oscillatory and rotational rheology. To investigate the underlying mechanism, we employ a combination of dissolution tests and nuclear Overhauser enhancement spectroscopy (NOESY). We believe that the use of such molecular hooks may pave the way for a wide range of soft materials with enhanced stability and mechanical properties. Noticeably, the presented materials are synthesized without the use of covalent cross-linkers, thereby improving processability by allowing their complete dissolution if desired.

Results and discussion

Following our previous study,[11] we used free-radical polymerization (FRP) with acrylamide (AAm) as the monomer and the thermoinitiator VA-044 to obtain highly entangled hydrogels. Polymerizations were carried out at 70 °C and in NMR tubes as molds (Fig. 1; for details see the SI). Concentrations were set to [AAm] = 2 M and [VA-044] = 0.005 mol% (referring to the monomer) to obtain UHMW polymers, which were measured to be around 3–4 MDa (Fig. S1). Correspondingly, the final polymer content per gel was 14 wt% (or 0.142 g mL^{-1}), which was two orders of magnitude higher than the critical overlap concentration of polyacrylamides of similar molecular weight.[11] Upon unmolding, cylindrical pAAm hydrogels were obtained; yet, despite exhibiting gel-like features, they generally started to flow within 30 min after being unmolded (Fig. 1b).

To introduce an additional kinetic barrier into the highly entangled polymer chains, we decided to modify the above formulation for FRP by including 1 mol% of PEGmeAc (M_n = 480 Da). In this rather coincidental finding, the resulting cylindrical gels were not only form-stable but also remained flow-resistant even after several months of storage (Fig. 1b). Importantly, the control gel, which was a blend of pAAm and 1 mol% poly(ethylene glycol) dimethyl ether (PEGdme, M_n = 500 Da), was not form-stable and flowed within minutes after being removed from the mold (Fig. 1b). These findings indicated that only in the presence of PEGmeAc, entanglements were trapped, resulting in stable flow-resistant networks.

After our initial observations of the flow-resistant samples, we hypothesized that the chains may be interacting electrostatically, causing a measurable change in the mechanical stability of the gels. Therefore, the poly(AAm-stat-PEGmeAc) copolymer hydrogels were subjected to uniaxial tensile tests.
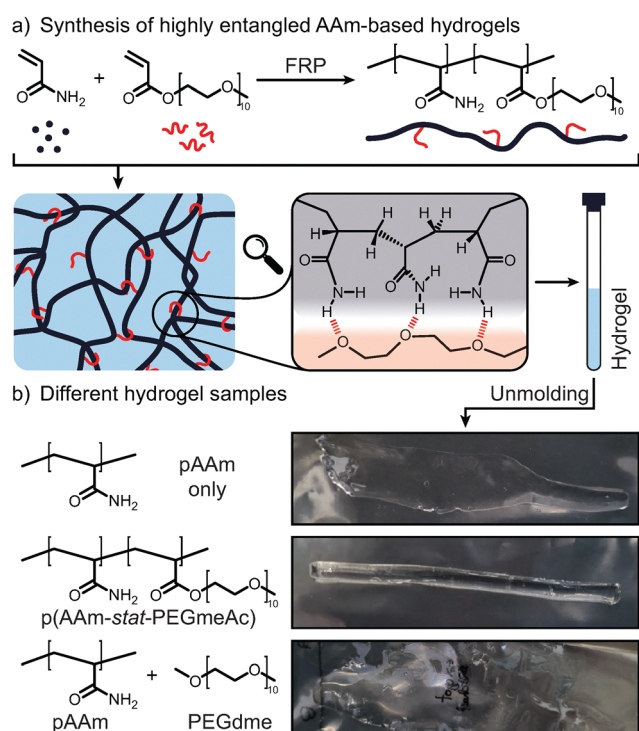

Fig. 1 (a) Synthesis of highly entangled AAm-based hydrogels showing the proposed mechanism and the role of PEGmeAc through hydrogen bonding and topological entanglements. (b) Different UHMW pAAm hydrogel samples obtained through thermo-initiated FRP: pAAm, the poly(AAm-stat-PEGmeAc) copolymer gel (1 mol%), and a blend of pAAm and 1 mol% PEG dimethyl ether (PEGdme).
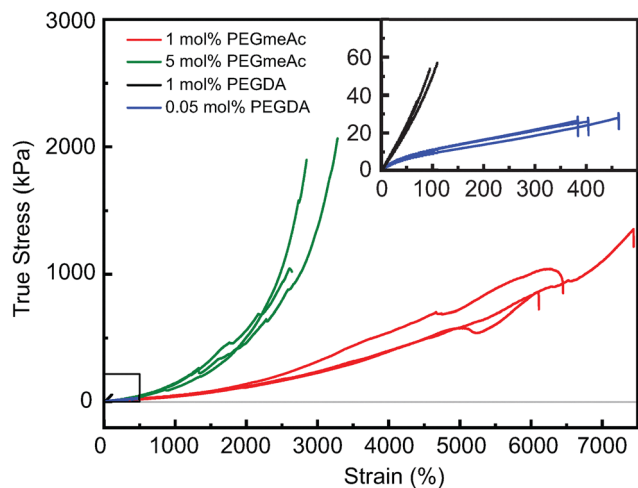
Fig. 2 True stress–strain curves measured through uniaxial tensile tests for pAAm hydrogel samples with 1 mol% PEGmeAc (red), 5 mol% PEGmeAc (green), 1 mol% PEGDA (black) and 0.05 mol% PEGDA (blue). The inset graph presents an enlarged window of the main graph (small box between 0 and 500% strain).

For this, cylindrical hydrogel specimens were glued into fixtures and the samples were extended with a strain velocity of 60 mm min^{-1} (Fig. S2).

It should be noted that samples without PEGmeAc flowed and could therefore not be tested. Excitingly, tensile tests of the poly(AAm-stat-PEGmeAc) hydrogels revealed extreme stretchability

(failure at $\varepsilon_f = 6600 \pm 600\%$), showing that energy was efficiently dissipated through the sliding of UHMW polymer chains (Fig. 2). In addition, for this sample (1 mol% PEGmeAc), a toughness (work of extension) of $W = 26 \pm 6$ MJ m^{-3}, a stiffness of $E = 6 \pm 1$ kPa and a strength of $\sigma = 1100 \pm 200$ kPa were measured (Fig. 2). Increasing the PEGmeAc content to 5 mol% reduced the stretchability to $\varepsilon_f = 2910 \pm 511\%$ and the toughness to $W = 12 \pm 3$ MJ m^{-3}, while stiffness ($E = 9 \pm 1$ kPa) and strength ($\sigma = 1700 \pm 500$ kPa) increased (Fig. 2). In contrast, substituting PEGmeAc with 1 mol% of poly(ethylene glycol) diacrylate (PEGDA, $M_n = 500$ Da) increased the gel stiffness ($E = 45 \pm 3$ kPa), but resulted in a brittle material with substantially reduced stretchability (failure at $\varepsilon_f = 90 \pm 16\%$) and toughness $W = 20 \pm 7$ kJ m^{-3}. This indicated that covalent cross-links immobilized UHMW chains to the detriment of the hydrogel's mechanical properties (Fig. 2 and Fig. S3, S4), while PEGmeAc side chains were able to stabilize the network and enabled full exploitation of the UHMW chains on the mechanical properties.

To decouple the effects of entanglement and PEGmeAc side chains, we performed two additional control conditions. To obtain a lowly-entangled gel with side chains, poly(AAm-stat-PEGmeAc) was prepared with 1 mol% PEGmeAc and 1 mol% VA-044, which afforded much shorter polymer chains of 92 kDa and 123 kDa, thus reducing the impact of entanglements. The obtained samples were more akin to viscous polymer solutions and could therefore not be tested on the tensile tester. To generate highly-entangled gels without side chains, pAAm samples with 0.05 mol% of PEGDA as the covalent cross-
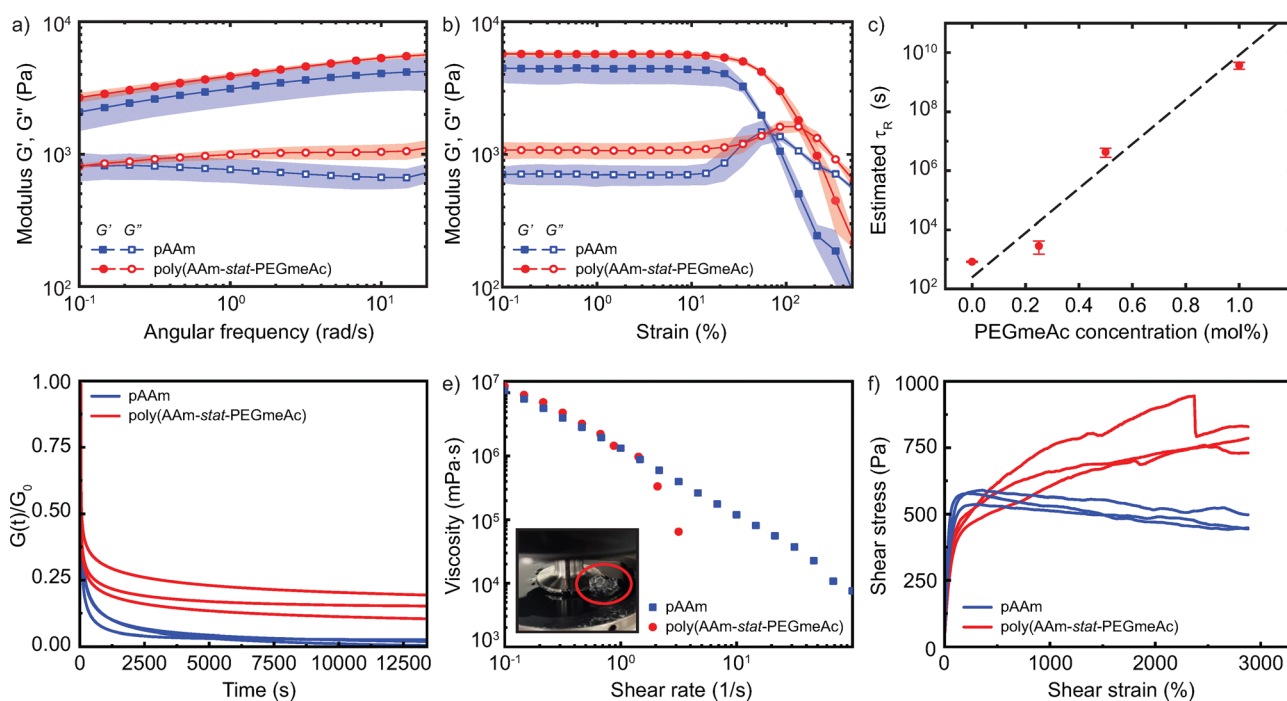

Fig. 3 Rheological comparison between pAAm and copolymer samples with 1 mol% PEGmeAc: (a) frequency sweep ($\omega = 100-0.1$ rad s^{-1}, $\gamma = 0.5\%$, $n = 3$), (b) shear strain sweep ($\gamma = 0.1-100\%$, $\omega = 10$ rad s^{-1}, $n = 3$), (c) estimated relaxation times for hydrogels with different concentrations of PEGmeAc, (d) stress relaxation modulus after applying 10% shear strain, (e) shear rate sweep ($\dot{\gamma} = 0.1-100$ s^{-1}) (the inset shows the image of the extruded sample), and (f) rotational shear experiments with increasing shear strain at a constant shear rate of 0.001 s^{-1}.

linker and 0.005 mol% of VA-044 were synthesized. According to Miyata *et al.*,[2] covalent cross-linking at concentrations below 0.1 mol% no longer dominates the mechanical properties and thus highly entangled networks can form. The resulting tensile curves (Fig. 2 and Fig. S5) showed that the entanglements led to increased stretchability (ε_f = 422 ± 61%) and stiffness (E = 20 ± 2 kPa) as compared to the covalent gels with 1 mol% of PEGDA. However, compared to the PEGmeAc-supplemented hydrogels, their toughness (W = 67 ± 19 kJ m^{-3}) and fracture strength (σ = 27 ± 4 kPa) were much reduced. Finally, initial cyclic tensile tests showed that the PEGmeAc-modified gels were largely recoverable, with residual strains indicating irreversible deformation after several cycles (Fig. S6). Overall, these results demonstrated that the mechanical properties of the hydrogels under uniaxial load only critically improved in the presence of both entanglements and PEGmeAc side chains.

To gain more insights into the role of pendant PEGmeAc within the UHMW poly(AAm-stat-PEGmeAc) hydrogels, we conducted rheological studies of the hydrogels. First, oscillatory frequency and shear strain sweeps were performed on the pAAm as well as poly(AAm-stat-PEGmeAc) hydrogels. For both materials, the storage moduli exceeded the loss moduli across the tested frequency range, the poly(AAm-stat-PEGmeAc) hydrogels were slightly stiffer (Fig. 3a). We also conducted strain sweeps to characterize the hydrogel's behavior at small and large amplitude oscillatory shear. At low shear strains, both conditions exhibited linear viscoelastic behavior (γ = 0.1–10%), while at large strains both materials entered the fluidized regime. A slight overshoot in the loss modulus was observed for both conditions, indicating the dissipative nature of the UHMW gels (Fig. 3b).

Next, the lowly-entangled gels with side chains as well as the highly-entangled gels without side chains were tested. For the former, the respective frequency sweeps showed strong frequency dependence with cross-over frequencies at ω = 0.3 and 68 rad s^{-1} for the samples with 123 kDa and 92 kDa, respectively (Fig. S7). This was expected, since both samples behaved like viscous polymer solutions and showed that the presence of PEGmeAc alone was not sufficient to induce gel stability. In contrast, the highly-entangled pAAm gel (without PEGmeAc) showed frequency-independent moduli over the entire measured frequency range, which is a classic signature of elastic permanent networks (Fig. S8). Furthermore, the storage modulus was much larger than the loss modulus (by a factor of 30), suggesting that most energy was stored elastically and only little energy was lost as heat. This is in contrast to the PEGmeAc gels (1 mol%), where the loss moduli were much higher (and frequency dependent), indicating a much more dissipative, viscous, and less elastic nature.

To investigate the influence of the amount of PEGmeAc on the stiffness of the hydrogels, we prepared additional hydrogel samples with 0.25, 0.5, 2.0, 5.0 and 10 mol% of PEGmeAc, this time again using 0.005 mol% of the initiator to ensure UHMW polymer chains were obtained (Fig. S9–S14). While samples with 0.5 mol% PEGmeAc reached the highest stiffness, the addition of 2.0 and 5.0 mol% PEGmeAc produced softer gels.

Surprisingly, a concentration of 10 mol% PEGmeAc resulted in similar moduli to that of the sample with 0.5 mol% (Fig. S9, S11, and S14). No clear trend could be determined, which indicated that multiple opposing effects were at play (*e.g.* additional cross-links *vs.* disrupting existing entanglements *vs.* increasing polymer concentrations).

To obtain a clearer understanding, we therefore sought to estimate individual relaxation times τ_R through extrapolation of the loss factor (tan δ), obtained from the frequency sweeps. For this, the lower frequencies were fitted to a simple power law and extrapolated to tan δ = 1, which designated the cross-over frequency and with this, the inverse relaxation time $1/\tau_R$ (Fig. S15). The obtained relaxation times increased from τ_R = 828 s for pure pAAm (0 mol% PEGmeAc) to τ_R = 2.85 × 10^3, 4.32 × 10^6, and 3.69 × 10^9 s, for 0.25, 0.5 and 1.0 mol% of PEGmeAc, respectively (Fig. 3c and Table S2). Beyond 1 mol% (2, 5, and 10 mol%), cross-over frequencies could not be extrapolated, leading to relaxation times approaching infinity. This indicated that increasing amounts of PEGmeAc drastically slowed down the chain dynamics until completely halted.

Additionally, to assess the thermomechanical properties, selected hydrogels containing 0, 1, and 10 mol% PEGmeAc were dried and measured using differential scanning calorimetry (DSC, Fig. S19 and S20). The glass transition temperature (T_g) of pure acrylamide is expected to be in the range of T_g = 150–180 °C.[18] The pAAm sample showed a value of T_g = 224 °C, which was higher, likely due to the highly entangled nature of the UHMW polymer chains. By introducing 1 or 10 mol% PEGmeAc, the T_g was reduced to 204 °C and 182 °C, respectively. This decrease was expected, as oligo ethylene glycol polymers are reported to have T_g < 0 °C.[19]

Overall, the findings suggest that PEGmeAc had little impact on the hydrogels' stiffness under small amplitude oscillatory shear (SAOS), yet increasing amounts of PEGmeAc increased their relaxation times to infinity, indicating a large contribution towards the sliding dynamics. To assess this contribution further and given that the high strain tensile tests showed dramatic differences in the mechanical properties, we decided to additionally employ rotational rheology to investigate the effect of PEGmeAc on the gel properties under large shear amplitudes.

Consequently, we performed stress relaxation experiments as well as rotational shear measurements for further characterization (Fig. 3d). If PEGmeAc indeed acts as a non-covalent cross-linker, the respective materials should show a more pronounced resistance to disentanglement under rotational shear as opposed to the pAAm samples. When recording the equilibrium relaxation modulus, significantly higher stiffness values were observed for samples with PEGmeAc (G_{eq} = 540 ± 50 Pa *vs.* G_{eq} = 120 ± 30 Pa), suggesting a greater elastic contribution towards network relaxation. When shear rate sweeps were performed, the pAAm hydrogel showed classic shear-thinning behavior, with the viscosity decreasing as the shear rate increased, likely due to the alignment of polymer chains (Fig. 3e). In stark contrast, poly(AAm-stat-PEGmeAc) underwent shear thinning only up to shear rates of $\dot{\gamma}$ = 1 s^{-1},

above which the hydrogels systematically extruded from the rheometer (Fig. 3e). In rotational shear tests, pAAm samples showed stress relaxation as the polymer chains disentangled, whereas poly(AAm-stat-PEGmeAc) exhibited increasing stress, with several samples failing mechanically during testing (Fig. 3f). Both rotational shear experiments clearly demonstrated that when PEGmeAc was incorporated, UHMW polymer chains strongly resisted chain disentanglement. Additionally, a strain-hardening effect was observed, which is in line with the enhanced friction of the side chains in low-density comb copolymers.[12]

To explain the enhancement in the mechanical properties of our poly(AAm-stat-PEGmeAc) copolymer hydrogels, we postulated the following mechanism (Fig. 1a): the ethylene glycol and the AAm repeating units in the polymer chains interact through the formation of hydrogen bonds.[11,20] These interactions promote and reinforce topological entanglements between the network polymers and the PEG side chains, making them act as mechanical hooks to stabilize the network in a non-covalent fashion.

To test this mechanism, dissolution assays were performed, where hydrogel pieces were immersed in excess of solute (at 1 wt%, n = 3) and their dissolution was monitored over time. Various aqueous conditions were applied, of which three different pH values were tested first (pH = 1, 7, and 14; Fig. 4). Varying the pH is known to catalyze ester hydrolysis and hence, if PEGmeAc is indeed responsible for reinforcing the network, its hydrolysis should accelerate the dissolution of the poly(AAm-stat-PEGmeAc) hydrogels.[21,22] While at pH = 14 poly(AAm-stat-PEGmeAc) copolymer gels dissolved within one day, their dissolution at pH = 1 took 7 days. This was likely due to the different kinetics of ester hydrolysis. In fact, similar PEG-based building blocks have been reported to hydrolyze faster at basic compared to acidic pH.[23] On top of this, any hydrolyzed ester groups will be deprotonated at basic pH, which will accelerate the dissolution of the gel through repulsive electrostatic interactions between carboxylate groups. Consequently, once the PEG chain was detached from the main backbone, its non-covalent interaction was lifted, promoting swift dissolution of the hydrogel. In contrast, when samples were immersed at neutral pH, dissolution was severely slowed down taking up

to 15 days; in fact, one sample remained undissolved for over 30 days. Regardless of pH, all pAAm control samples dissolved within 1 day (Fig. 4b). The dependence of the dissolution kinetics on pH confirmed that PEGmeAc played a key role in the cross-linking of the gels.

Secondly, the gel samples were immersed in highly concentrated solutions of sodium chloride and urea (both 5 M). Sodium chloride is known to disrupt polar/ionic interactions between the polymers through shielding their polar components, while urea breaks hydrogen bonds altogether.[24,25] For the sample with 1 mol% of PEGmeAc, the dissolution took 7 days in sodium chloride, halving the dissolution time compared to the samples immersed in pH-neutral water (Fig. 4a). Noticeably, when the gel samples were immersed in urea, dissolution took an average of 1.3 days. The pAAm control samples dissolved within one day for both NaCl and urea (Fig. 4b). These findings suggested that the PEGmeAc unit was actively engaged in hydrogen bonding to function as a non-covalent cross-linker. Noticeably, this way the hydrogels could also be disintegrated once they were no longer needed.

To provide spectroscopic evidence for hydrogen bonding between PEGmeAc chains and the AAm backbone, we performed NOESY experiments. Previous studies revealed that hydrogen-bonding complexes can be formed between PEG chains and polymeric acids (e.g., polyacrylic acid).[26–28] Such complexes have been shown to form either in solution or as water-insoluble resins depending on the polymer molecular weight and environmental conditions (e.g., pH and salts). Given that pAAm is also known to engage in hydrogen bonding, we conducted gradient selected 1D NOE experiments on our hydrogels at AAm concentrations of 2 M or 14 wt% to verify whether PEG groups interacted with the polymer network (Fig. 5b–d).[29–32] To begin with, the ^{1}H NMR spectrum of a poly(AAm-stat-PEGmeAc) copolymer hydrogel was recorded (Fig. 5a). The spectrum showed three important signals, two broad singlets at δ = 7.65 and 6.91 ppm corresponding to the AAm protons and a singlet at δ = 3.61 ppm for the ethylene glycol repeating units.

When either the NH$_2$ or ethylene glycol proton frequencies are selected for inversion to conduct a gradient selected 1D NOE experiment, other protons should only experience NOE effects if they are in close proximity to the protons that are selected for inversion. As can be seen from Fig. 5b, such NOE effects were clearly observed for the poly(AAm-stat-PEGmeAc) copolymer gel. Each NH$_2$ proton produced a NOE signal for the ethylene glycol units of PEGmeAc at δ = 3.61 ppm when selected for inversion. Conversely, when the ethylene glycol signal at δ = 3.61 ppm was selectively inverted, both NH$_2$ protons showed a NOE effect, confirming their close spatial proximity and hence the formation of hydrogen bonds (similar observations were made in pure water; Fig. S21).

As a control, we also prepared pAAm hydrogels blended with 1 mol% of PEGdme (Fig. 5c). In this composition, PEGdme should in principle be able to form hydrogen bonds, but unlike PEGmeAc, it is not copolymerized into the polymer backbone. The resulting spectra showed that regardless of the proton
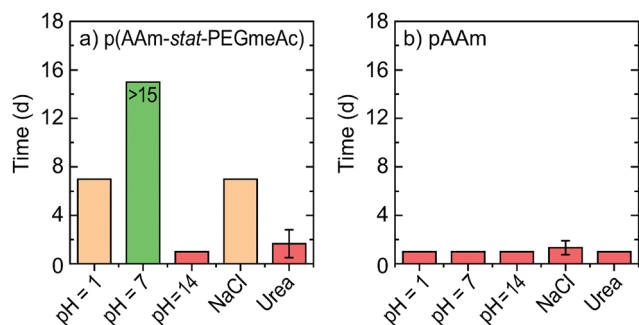

Fig. 4 Dissolution assays (n = 3) of highly entangled hydrogels: (a) poly(AAm-stat-PEGmeAc) and (b) pAAm, in water with pH = 1, 7, and 14 as well as NaCl$_{(aq)}$ (5 M) and urea (5 M).
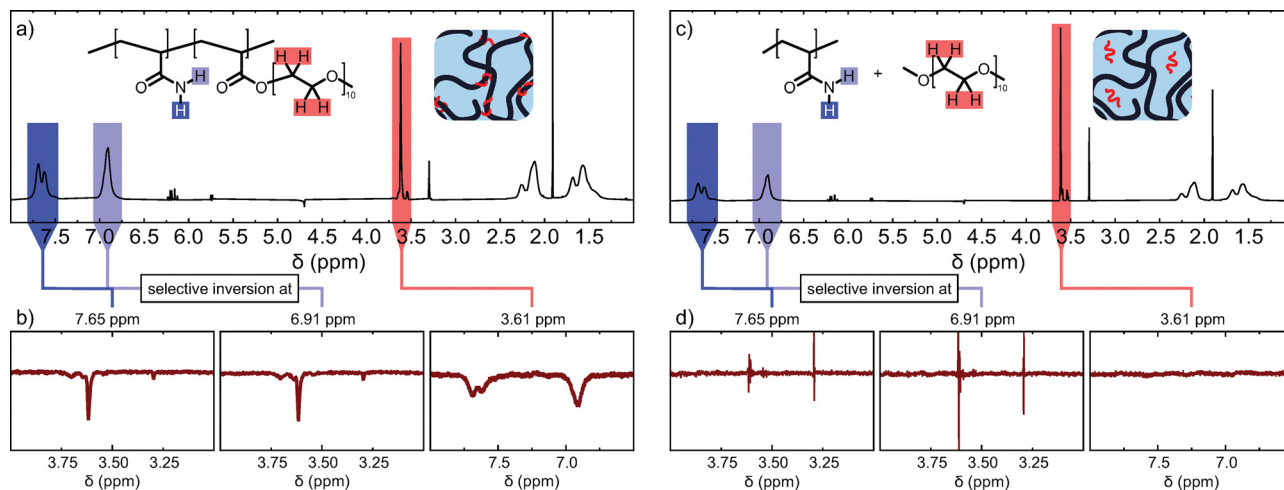
Fig. 5 ^{1}H NMR spectra of (a) poly(AAm-stat-PEGmeAc) and (c) poly(AAm) blended with 1 mol% PEGdme, recorded in a 95:5 mixture of 50 mM acetate buffer and D$_2$O. Excitation sculpting was used to suppress residual solvent signals. Gradient selected ^{1}H NOE experiments (mixing time d_8 = 0.1 s) for (b) poly(AAm-stat-PEGmeAc) and (d) poly(AAm) blended with 1 mol% PEGdme when selectively inverted at δ = 7.65, 6.91, and 3.61 ppm, respectively. No ^{1}H NOE effects were observed upon selective inversion of the blend.

frequency selected for inversion, respective NOE signals were not detected (Fig. 5d).† This finding was consistent with previous studies, which reported stronger complexation in copolymers compared to homopolymer mixtures.[29] This effect can be attributed to reduced losses in translational entropy when PEG groups are already grafted to polymer chains, resulting in a more favorable free energy of binding. In addition to not being able to form hydrogen bonds, PEGdme groups could also not act as mechanical hooks since they were not copolymerized into the network. As a result, respective samples rapidly flowed after unmolding, highlighting the importance of topological entanglements in the system. The above findings therefore showed that PEGmeAc had to be copolymerized into the network to interact with surrounding network strands via hydrogen bonding, promote the formation of topological entanglements and stabilize the network.

To assess this network stabilization caused by the molecular hooks, we hypothesized further that the hydrogen bonds between the PEGmeAc and pAAm chains created an energetic barrier to the motion and disentanglement of chains. If the total amount of these additional bonds between two entanglements is collectively modeled as one effective bond, chain motion and disentanglement requires breaking this effective bond. Therefore, the energetic barrier linked to its dissociation should scale linearly with the concentration of PEGmeAc side chains. Since the relaxation time in dynamic networks is proportional to the characteristic lifetime of a bond (and hence the inverse of the rate of bond detachment), we used the relaxation times from Fig. 3c to calculate this activation energy.[33–35] Using the Eyring equation, the enthalpy for the detachment of this effective bond (per mol% PEGmeAc) was calculated to be 128 kJ mol^{-1} (for details see the SI).

To further show that this energy indeed corresponded to the activation energy of the bonds formed between PEGmeAc and pAAm, we measured τ_R for a gel with 1 mol% PEGmeAc at

different temperatures ranging from 5 to 50 °C (Fig. S16). Next, an Eyring plot was constructed to extract the activation enthalpy (Fig. S17).[36,37] The latter was calculated to be 144 kJ mol^{-1}, which was in line with the value found for varying mol% concentrations of PEGmeAc (Fig. 3c; for details see the SI). Together, these findings suggested that (i) PEGmeAc chains create additional interactions causing an energy barrier against the motion and disentanglement of pAAm chains and (ii) this activation energy is proportional to the density of PEGmeAc side chains in the network. Consequently, the presence of the PEGmeAc molecular hooks resulted in a major stabilization of the hydrogels and an enhanced resistance to deformation, shear, and disentanglement.

Conclusions

To sum up, we reported on poly(AAm-stat-PEGmeAc) copolymer hydrogels that show extreme stretchability (6600%) as well as enhanced toughness (26 MJ m^{-3}). We found that the incorporation of minor quantities (1 or 5 mol%) of PEGmeAc into a highly entangled (and UHMW) pAAm polymer backbone resulted in stable, flow-resistant hydrogels. Relevant control samples such as pure pAAm as well as blends of pAAm and PEGdme flowed after the samples were removed from the mold. Samples were tested under uniaxial tensile stress, oscillatory shear, and rotational shear. Although the mechanical properties were similar in the oscillatory mode, the determination of relaxation times and rotational shear rheology confirmed that the incorporation of PEGmeAc introduced a major barrier for the polymers to disentangle as compared to samples without it. Respective samples extruded systematically, while pAAm control samples showed standard shear-thinning behavior and flow. Mechanistic investigations confirmed that the effect originated from hydrogen bonding and topological

entanglements. Dissolution assays and NOESY experiments revealed that PEG groups interact with pAAm chains from the backbone through hydrogen bonding, reinforcing topological entanglements to create stable, flow-resistant hydrogels with enhanced mechanical properties. Furthermore, by using the relaxation times, we were able to calculate enthalpy values representing the energetic barrier posed by the molecular hooks within the network. Within the area of hydrogels, the current strategy could serve as a promising tool to induce structural integrity into highly entangled hydrogels, while maintaining purely non-covalent nature. In the future, we aim to translate this concept to a broad range of polymers that engage in hydrogen bonding and study its effectiveness in enhancing material properties. In fact, preliminary data have shown that poly(hydroxyethyl acrylamide) (pHEAm) slightly stiffened in the presence of 1 mol% PEGmeAc (although extracted relaxation times were similar, Fig. S18).‡ We believe that the combination of UHMW polymer chains with small hydrogen bond-facilitating units such as PEGmeAc represents a simple and low-cost method to enhance the mechanical properties of a variety of soft materials. Hence, prospective investigations will concentrate on leveraging this effect.

Author contributions

Conceptualization: SM; data curation: EA, LC, SM; formal analysis: EA, LC, MWT, SM; funding acquisition: SM; supervision: SM; writing – original draft: EA, SM; writing – review & editing: EA, LC, MWT, SM.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: **https://doi.org/10.1039/d5mh01344e**.

The data underlying this study are openly available at the ETH Research Collection (**https://www.research-collection.ethz.ch/**, DOI: **https://doi.org/10.3929/ethz-b-000745535**).

Acknowledgements

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† The only observed signals are out-of-phase and exhibit line widths that do not match those of the polymer. Therefore, they are artifacts and do not represent the actual NOE effects of the respective protons.
‡ Pure poly(acrylic acid), poly(methacrylic acid) and poly(hydroxyethyl methacrylate) were also tested, but could not be analyzed due to precipitation or syneresis of the formed hydrogels under the employed reaction conditions.

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