Unusual Aspects of Supramolecular Networks: Plasticity to Elasticity, Ultrasoft Shape Memory, and Dynamic Mechanical Properties

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Supramolecular bonds have been widely used for designing polymers because of their reversible nature. In contrast, utilization of their dynamic equilibrium nature to access materials of unusual mechanical properties has been poorly explored. Taking full advantage of this latter attribute requires the design of polymer networks with high contents of supramolecular bonds. In this work, polymer networks with high contents of self-complementary hydrogen bonds (ureidopyrimidinone) are synthesized using thiol–acrylate click addition. The excellent tunability of the network allows a range of intriguing mechanical properties to be achieved including the transition from plasticity to elasticity, ultrasoft shape memory polymer, strong strain rate dependence, and high mechanical damping. Materials with such versatile dynamic behaviors may open up a range of new applications.

1. Introduction

Utilization of noncovalent bonds to build polymer materials is the basis of supramolecular polymer chemistry. The unique specificity and reversibility of the supramolecular bonds in comparison to traditional covalent bonds serve as the important basis for self-assembled polymer systems and diverse stimuli-responsiveness of the resulting polymers.[1–3] Besides that, supramolecular bonds are dynamic in nature and they typically exist in equilibriums, that is, the bonds constantly undergo breaking and reforming at timescales characteristic to the particular bonds. Despite the wide recognition of the equilibrium nature of supramolecular bonds, taking advantages of such a unique attribute in particular its relative timescale in designing materials of unusual macroscopic properties remains poorly explored.

Among all supramolecular bonds, hydrogen bonding has received most attention owing to its wide existence. In particular, the discovery of the self-complementary hydrogen bonding by ureidopyrimidone (UPy) structural units, due to their exceptional bond strength, has pushed the development of supramolecular science.[1] Of equal importance is that the rate of its reversible breaking and reforming seems to match the timescale that is relevant for macroscopic mechanical properties of polymers. As such, UPy has been elegantly utilized to design polymers with enhanced mechanical performances by virtue of its energy dissipation characteristics.[4] Similarly, its equilibrium nature allows molecular rearrangements as a way to relax detrimental stresses often encountered in the solidification of polymer coatings.[5] Additionally, the temperature dependence of the dynamic equilibrium permits freezing/activating the UPy bond dynamics by temperature variation, which has been proven useful in designing shape memory polymers[6–8] and reversible adhesives.[9,10]

In principle, the dynamic equilibrium nature of UPy may also be particularly suitable for designing materials with strain rate dependent mechanical properties, as suggested by a recent rheological study by Anthamatten and co-workers.[11] As one would expect, the magnitude of the strain rate dependence should be proportional (not necessarily linearly) to the UPy content in the polymer network. Unfortunately, the above study was limited to covalently crosslinked elastomers with low UPy contents due to the practical difficulty in introducing more UPy units in the synthesis. Aside from this practical issue, what is not readily obvious is that even if more UPy can be incorporated in a covalent network, at a threshold UPy content the permanent network established by the covalent linkages would be lost. Thus, we believe there is an upper limit of UPy content in an elastomer network above which an elastomer would transition into a more liquid-like state, perhaps with unusually high viscosity due to the ample transient supramolecular UPy linkages.

We further note that strain rate dependence is common for polymers, but such an effect is typically too weak. Only those that exhibit strong strain rate dependence are of great interest, that is, what matters is the magnitude. From practical standpoint, the strain range within which the rate dependent mechanical properties are achieved also needs to be relevant. A prime example meeting both criteria is the so-called shear thickening fluid. Viscosity of a shear thickening fluid changes dramatically when a force is applied quickly (i.e., high strain rate), even transform from a liquid state to a solid-like state. This has led to the design of body armor that is flexible under normal circumstance (low strain rate conditions) but can significantly stiffen to provide protection against ballistic attacks (high strain rate conditions).[12] Such a strong non-Newtonian

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behavior is typically observed for various fluids including suspensions, associative polymers, worm-like micelles, and polymer solutions.[13] The fluid nature, however, is a major limitation for many practical uses due to the need for additional containment.

In this work, we aim to design covalently crosslinked elastomers with high UPy contents to maximize their dynamic mechanical properties without losing its solid elastomeric nature. The dynamic equilibrium nature of UPy binding is expected to serve as the mechanistic basis for the dynamic mechanical properties. When a force is applied slowly (a low strain rate), the UPy dimers have sufficient time to break and reform, thus do not contribute to the overall crosslinking. Under this condition, the network should exhibit a low modulus since only the covalent crosslinks are effective. When a force is applied quickly (a high strain rate), however, the timescale may be sufficiently short such that the UPy dissociation and re-association is practically negligible,[14] the links provided by UPy dimers contribute to the overall effective crosslinking in addition to the covalent crosslinks. Thus, the elastomer should be stiffer. Hereafter, the design and synthesis of the supramolecular networks with high UPy contents as well as their dynamic mechanical properties are reported.

2. Results and Discussion

We chose to use the base catalyzed thiol-acrylate reaction between a multi-thiol monomer (pentaerythritol tetrakis(3-mercaptopropionate), PTME) and two acrylate monomers (UPy containing acrylate (UPyA) and poly(ethylene glycol) diacrylate (PEGDA)) (**Figure 1**) to synthesize the polymer networks. The molecular weight of PEGDA was ≈700 g mol^{-1}, small enough to avoid room temperature crystallization of the PEG chains. The click nature of thiol-acrylate reaction allows more precise structural control, leading to better uniformity of the networks versus the radical initiated polymerization that can otherwise also be employed for the network synthesis.[15] A series of networks (**Table 1**) were synthesized by varying the molar ratio between the UPyA and PEGDA monomers while maintaining the overall stoichiometric balance between thiol and acrylate, i.e., the thiol–acrylate ratio being 1:1 for all the samples. The samples were denoted as UPyX with "X" being the molar percentage of acrylate from UPyA versus the total acrylate from both UPyA and PEGDA. Here, we should note that UPyA contains one acrylate unit whereas PEGDA has two acrylates per molecule.

Under the reaction conditions, acrylate typically reaches full conversion as evidenced by the disappearance of acrylate

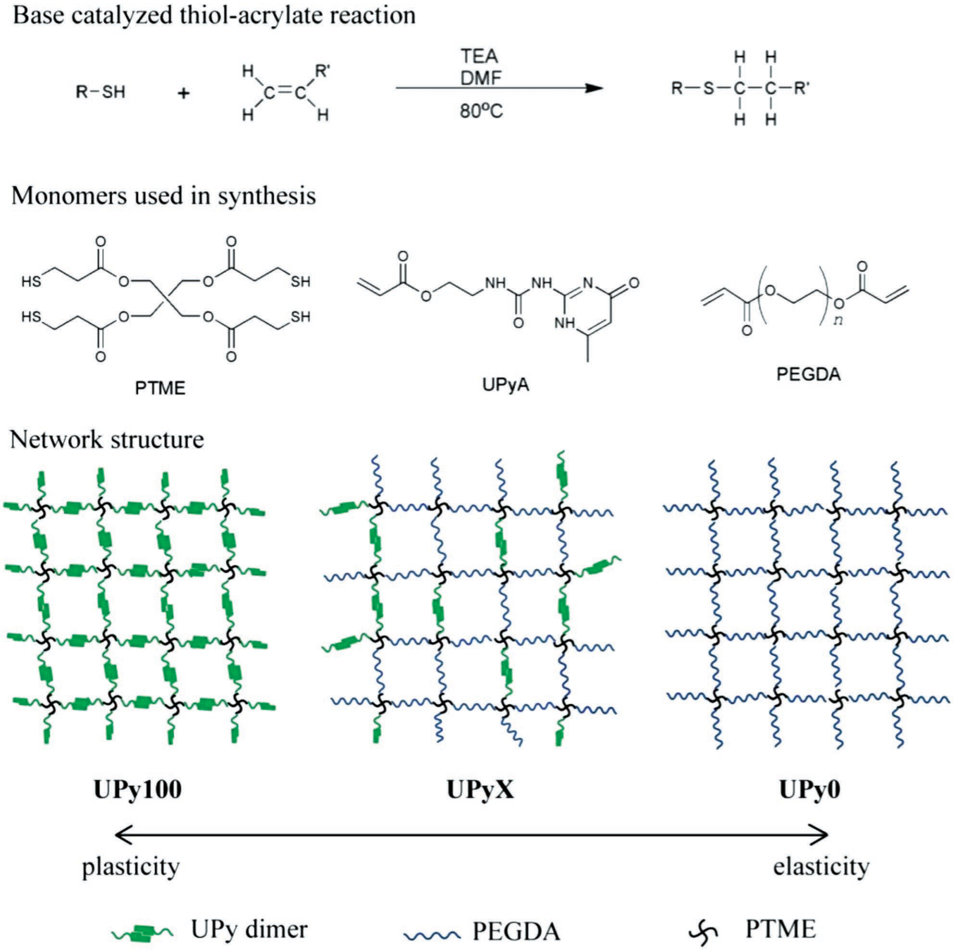

Figure 1. Network design and synthesis.

Table 1. Supramolecular UPy networks: compositions, plasticity to elasticity transition, and shape memory performance.

Sample	R_f [%]	R_r [%]	State
UPy100	–[a]	–[a]	Plastic
UPy75	–[a]	–[a]	Plastic
UPy50	100.0	11.6	Plastic[b]
UPy40	99.4	100.0	Elastic
UPy30	94.7	99.1	Elastic
UPy25	65.7	99.7	Elastic
UPy10	0	99.9	Elastic
UPy0	0	99.0	Elastic

[a] Sample **UPy100** and **UPy75** could not be tested for their shape memory performance because they flew at elevated temperature; [b] **UPy50** had a strong tendency to flow in the test as it could be stretched to 200% even under the very small preload force of 0.001 N. Note: **UPy40**, **UPy30**, and **UPy25** were evaluated at a strain of ≈50%. **UPy10** and **UPy0** were evaluated below its maximum strains (<50%).

double bond in the NMR spectrum of an exemplary sample **UPy40** (Figure S1, Supporting Information). The cleanness of the click reaction allows the suppression of the acrylate self-polymerization, thus the network structure can be schematized as Figure 1. For **UPy100**, all the crosslink points are UPy dimers. Such a network is expected to be transient in nature since all the crosslinks are at a dynamic equilibrium state. Since the UPy dimers are exchangeable bonds, we expect **UPy100** to exhibit plasticity, referring to the ability of a network to relax stress upon deformation and thus undergo permanent deformation.[16–18] The exchange rate is slow at low temperatures and faster at elevated temperatures. On the other extreme is **UPy0**, all the crosslinks are permanent covalent bonds, it is essentially a conventional crosslinked elastomer that is expected to show elasticity, i.e., deformations are reversible.

In between **UPy100** and **UPy0** with various amounts of UPy in the networks, the transient UPy crosslinks and permanent covalent crosslinks co-exist. However, a true permanent network can only be established when the permanent crosslinks start to percolate throughout the entire network at a critical concentration (gelation). We thus expect a transition from plasticity to elasticity at a threshold UPy molar percentage. To probe such, all the samples were subjected to typical shape memory tests. In such a test, the sample was deformed at 70 °C and cooled down to 10 °C under the deformation force. Subsequent releasing the force allowed evaluation of the shape fixity. Strain recovery was conducted by further heating to 70 °C under a force free condition. The shape fixity and recovery ratios thus obtained are reported in Table 1. The results show that the shape fixity has a strong dependence on the UPy content. This is not surprising as the thermal transition associated with UPy provides the mechanistic basis for its shape fixing capability. What is more relevant for the purpose of this study is the shape recovery ratios. **UPy100** and **UPy75** could not be tested for shape memory functions as they flew at the elevated temperature due to the lack of permanent network structures. On the other extreme is **UPy0**, which is a conventional covalent elastomer without shape fixing function in the tested temperature range, thus its shape recovery cannot be evaluated by a shape memory test. However, as one would expect, **UPy0** is purely elastic as any stretch would recover upon removal of the stretching force. Whereas all the samples were subjected to shape memory tests, we should note that materials show shape memory functions only within a particular network composition range (**UPy40**, **UPy30**, and **UPy25** in Table 1). Selected quantitative shape memory cycles for **UPy50**, **UPy40**, and **UPy25** are shown in **Figure 2** for direct comparison. **UPy40** and **UPy50** both exhibit near perfect shape fixing capability. However, the shape recovery for **UPy50** is quite minimal, suggesting that the deformation is very much plastic. The shape recovery ratio improved to nearly 100% as the UPy content is reduced to 40% or below, indicating that a sufficient level of covalent linkages allowed establishing permanent networks. The shape fixity, on the other hand, increases with the UPy content. As the UPy content falls below 30, the shape fixity decreases as the network UPy content reduces (Table 1). These results indicate the essential role of the UPy in ensuring good shape fixity. The shape fixing and recovering ability of samples **UPy25**, **UPy40**, and **UPy50** are further demonstrated in Figure 2d, showing visually the perfect shape fixity for **UPy50** and **UPy40** and poor shape fixity for **UPy25**, but complete recovery only for **UPy40** and **UPy25**. Overall, only **UPy40** and **UPy30** show ideal shape memory behaviors with shape fixity and recovery both approaching 100%. Although the primary purpose here was to probe the plasticity/elasticity, data in Table 1 do systematically establish the composition range in which UPy containing polymer networks should exhibit optimal shape memory performance. The results explain the differences in shape memory performances for various UPy systems reported in the literature.[6–8,11]

Regardless of the shape fixity, it is the shape recovery ratio that determines the plasticity/elasticity. Although **UPy100** and **UPy75** could not be tested for shape recovery, the fact that they flow upon heating indicates that any deformation is permanent, thus they show plasticity. The shape recovery ratio for **UPy50** is near zero, also indicating plasticity. On the contrary, **UPy40**, **UPy30**, **UPy25**, and **UPy0** show pure elasticity since they all recover fully. The results imply that the plasticity/elasticity transition occurs at a composition between **UPy40** and **UPy50**.

We believe this threshold plasticity/elasticity transition point is strongly related to the gel point commonly known for any other covalently crosslinked network as both are tied to the formation of a percolating network. As such, the transition point should be predictable by the statistical Flory theory.[19] According to this theory, the gel point for a network condensed from bifunctional units AA, BB, and polyfunctional units A_f can be expressed as Equation (1)

$$P_g = \frac{1}{\left[r + r\rho(f-2)\right]^{1/2}} \tag{1}$$

where f is functionality of the branching units, r is the ratio between A and B functional groups, and ρ is the ratio of A's in A_f to the total number of A's in the mixture. For **UPy0**, the reaction is between a tetrathiol (A_4) and a diacrylate (BB) in the stoichiometric balance. Thus, $r = 1$, $\rho = 1$, and $f = 4$, the gel point as calculated from the above equation is 0.58. From the standpoint of permanent network formation, replacing diacrylate in **UPy0** with UPyA is equivalent to reducing the reaction conversion

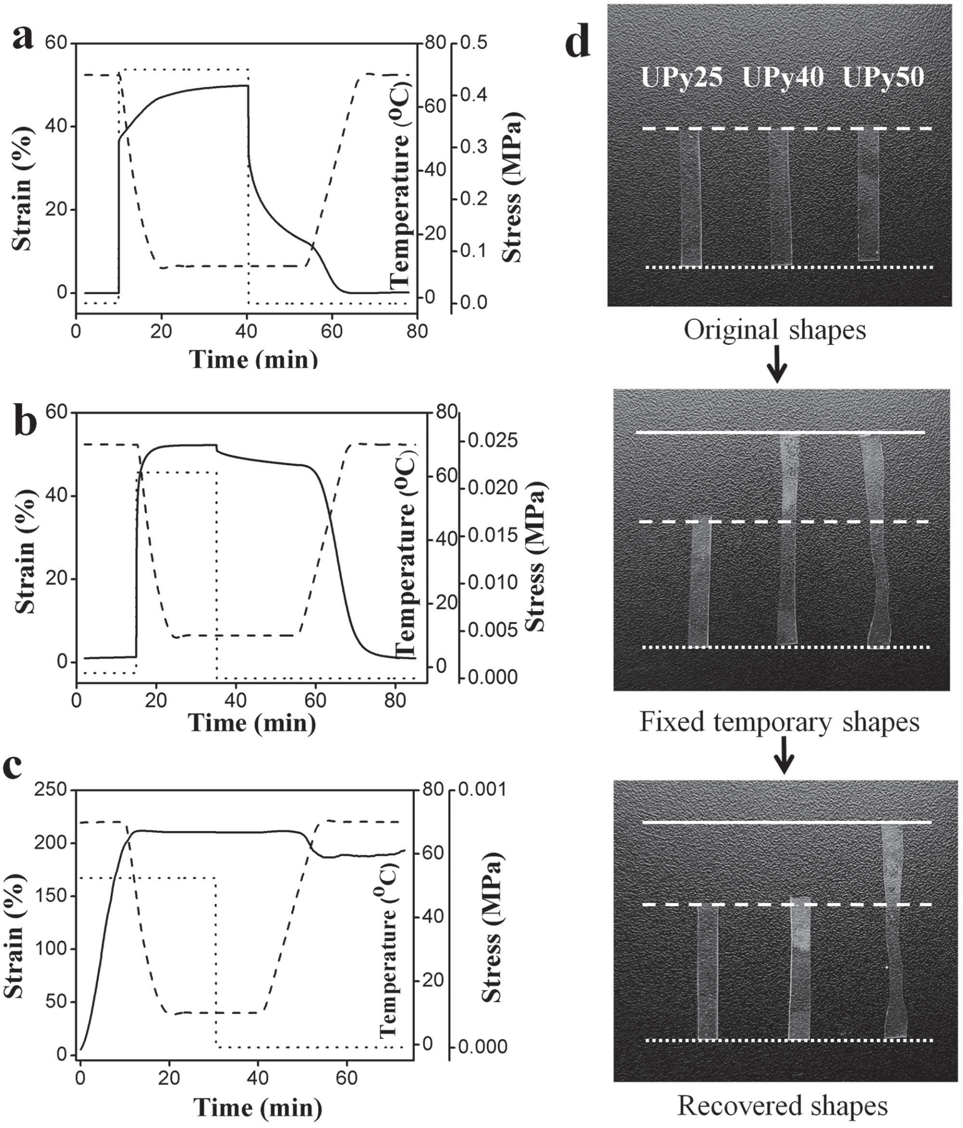

Figure 2. Quantitative shape memory cycles for supramolecular UPy networks of a) **UPy25**, b) **UPy40**, and c) **UPy50** (—strain; ----temperature; ····· stress). d) Visual demonstration of the shape memory performance for supramolecular UPy networks.

since the latter does not contribute to the permanent network. We thus conclude that the transition from elasticity to plasticity for our hybrid supramolecular network should occur when 42% of acrylate in **UPy0** is replaced by UPyA. In essence, the theory predicts that the plasticity/elasticity transition occurs at **UPy42**, in an excellent agreement with the experimental results. Here, the use of click based thiol-acrylate reaction in designing the networks plays an important role as it ensures the network homogeneity and thus the good fit with the theoretical prediction.

We emphasize here again that plasticity here refers to the ability of materials to undergo permanent irreversible (non-recoverable) deformation. The driving force for deformation recovery is typically entropy. Aside from polymer melts that can flow under forces to relax the stress and undergo deformation without change the entropy (thus permanent deformation), polymer networks exhibiting plasticity via exchangeable covalent crosslinks have drawn great attention lately.[2,16,18] This latter plasticity arises from the ability of the network to undergo topographic rearrangements to relax stress/maintain constant entropy during deformation. The plasticity observed for our UPy containing networks originates from a similar mechanism, except that the bond exchanges occur between the supramolecular UPy dimers instead of reversible covalent bonds. In principle, the compositional dependent plasticity to elasticity transition observed for our UPy containing networks can be extended to polymer networks with permanent and exchangeable covalent crosslinks.

The UPy networks exhibiting plasticity bear characteristics of polymer melts in that they do not have fixed permanent shapes although the samples do appear more like elastomers at room temperature due to the slow dimer exchange. Their somewhat fluidic nature becomes more obvious at elevated temperatures as the dimer exchange becomes faster. We expect these networks to exhibit strong dynamic mechanical properties owing to their high UPy contents. This is supported by the rheology test results shown in Figures S2–S4 (Supporting Information). As mentioned in the Introduction, however, solid polymers with strong dynamic mechanical performance are rare and in fact more challenging to make relative to strain rate dependent fluids. For this reason, we focus below on the dynamic mechanical performance of the elastic samples with UPy contents below 40%. For reference, the dynamic mechanical analysis (DMA) curve for a representative sample **UPy40** is provided as Figure S5 (Supporting Information).

Hereafter, we elected to use static mechanical tests at fixed strain rates to study the mechanical properties of the various elastomers. The choice of such over dynamic mechanical tests at different frequencies was because the former are more directly relevant for the mechanical performance in the actual use of solid polymers. The dynamic aspect of the mechanical performance was probed by varying the strain rate or temperature for each test. **Figure 3**a shows the strain rate dependence of the modulus of the various samples. **UPy0** exhibit negligible strain rate dependence when the strain rate changes from 10 to 10 000% min^{-1}. By comparison, both **UPy25** and **UPy40** show strong strain rate dependence. The stress–strain curves of **UPy40** in a low strain range with varied strain rates are presented in Figure S6 (Supporting Information). For this particular sample (**UPy40**), its modulus increases from 295 kPa (strain rate: 10% min^{-1}) to 4042 kPa (strain rate: 10 000% min^{-1}). This 14 times modulus increase is significantly higher than that of a polymer network with a much lower UPy content, within a similar strain range.[11] Here again, the strain rate dependence arises from the relative timescale of the UPy association/disassociation kinetics versus the rate at which the strain is applied and magnitude is strongly dependent on the UPy content.

Figure 3b shows the temperature dependence of the various elastomers. The modulus of the pure covalent elastomer (**UPy0**) increases slightly with temperature, which is fully expected due to entropy elasticity.[20] In contrast, the modulus of **UPy25** appears to be temperature independent, indicating that the enthalpic contribution of the UPy starts to impact the modulus. A large temperature impact is observed for **UPy40** and the temperature dependence of its modulus at different strain rates is presented in Figure S7 (Supporting Information). At a low strain rate of 10% min^{-1}, for instance, its modulus drops significantly with temperature: from 295 kPa (25 °C) to 58 kPa (85 °C). This behavior originates from the fact that the UPy dimer exchange becomes fast at elevated temperatures, as such the UPy units effectively contribute less to the modulus.[7] It is noteworthy that the modulus of 58 kPa (85 °C) for **UPy40** is significantly lower than those of typical covalent elastomers (usually above several hundreds kPa). We note here that dry elastomers (i.e., solventless) that match the softness of biological tissues (e.g., the modulus of muscle is around 10–100 kPa[21] are highly desirable for various biomedical applications. However, materials with such softness are challenging to make due to the intrinsic contribution of chain entanglements in lightly crosslinked elastomers. Although the softness of **UPy40** is observed at a temperature much higher than biologically relevant temperatures, the underlying mechanism seems to suggest a potential way to achieve ultrasoftness. Along with its perfect shape memory performance, **UPy40** represents an interesting example of an ultrasoft non-gel-based SMP.[22–26]

The dynamic exchangeable nature of the UPy bonds offers an intriguing mechanism for mechanical damping. This is demonstrated in free falling experiments using balls made of **UPy0**, **UPy25**, and **UPy40**. **Figure 4** captures the starting positions and the peak positions in the first two bounces of each ball. The left and right columns correspond to the experiments conducted at room temperature and 80 °C, respectively. The pure covalent ball **UPy0** bounced to peak heights that were relatively close to the starting position and the peak positions were not affected much by the temperature increase. By contrast, the peak heights for **UPy25** were noticeably lower, demonstrating its better mechanical damping which can be further enhanced at the elevated temperature as implied by the additional reductions in peak heights. The damping performance and its temperature dependence were maximized in **UPy40** with the highest UPy content while maintaining its elasticity. In particular, the second peak height in the 80 °C experiment was close to zero. Again, the superior damping performance arises from the UPy dynamics. Its equilibrium nature allows bond exchanges at a timescale relevant for the free fall experiments. As such, bond exchange occurs upon impacting the ground but recovers to the original bonding pairs driven by the overall elasticity. In such a process, the bond exchange and recovery functions more like molecular friction, the macroscopic

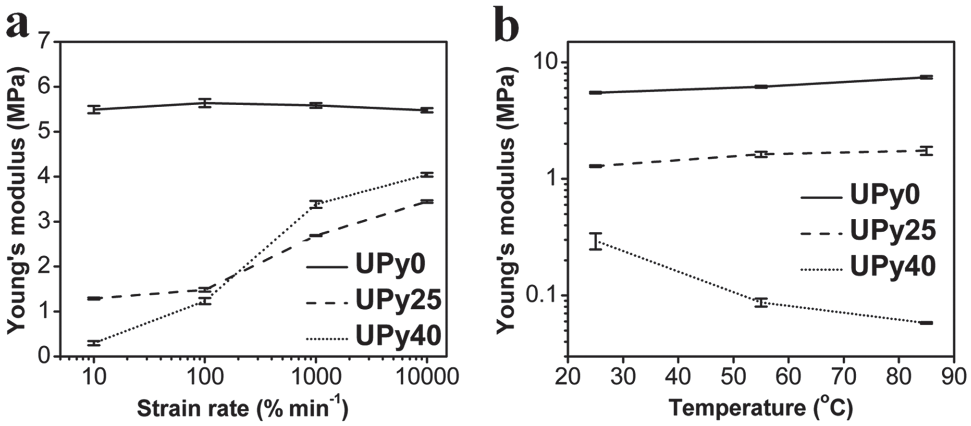

Figure 3. Dynamic mechanical properties. a) Strain rate dependence at 25 °C and b) temperature dependence (strain rate: 10% min^{-1}).

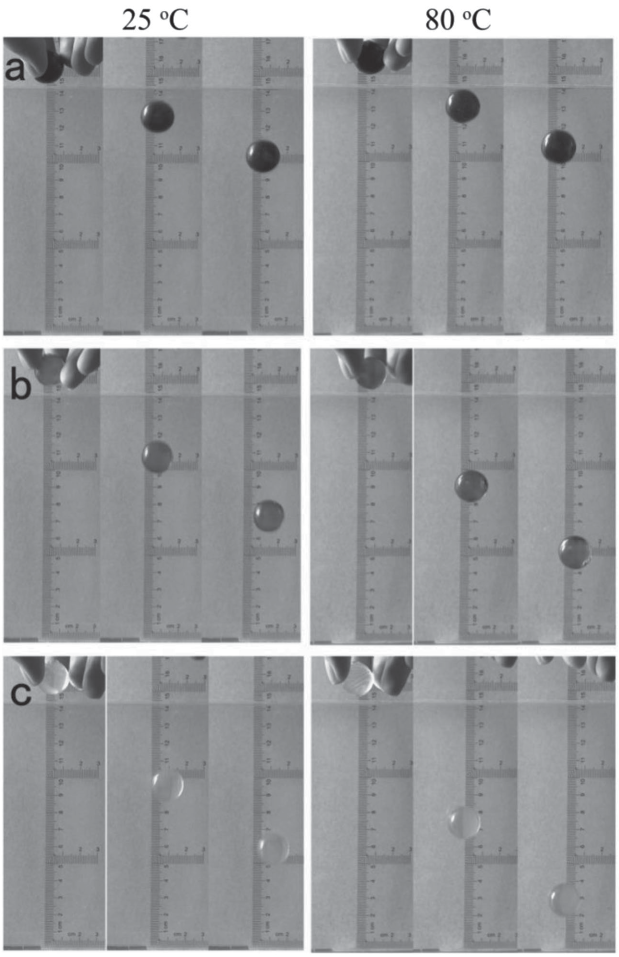

Figure 4. Mechanical damping performance. a) **UPy0**, b) **UPy25**, and c) **UPy40**. Balls are colored differently for distinction.

mechanical energy is thus consumed, leading to its damping behavior. Here, faster bond exchange at the elevated temperature allows dissipation of more mechanical energy within the given timescale, leading to better damping.

In theory, lowering the molecular weight of PEGDA can lead to a higher UPy content in the network, which should lead to more pronounced dynamic mechanical behavior. In practice, however, this will increase the risk of phase separation during the network synthesis owing to the poor solubility of UPy. In addition, more covalent linkages will need to be accordingly introduced in the network to ensure that the obtained material maintains its elastic solid nature. This will unavoidably decrease the maximum strain, i.e., material will become more brittle. Thus, the best balance between the dynamic mechanical property and brittleness will need to be evaluated case by case based on application requirements.

3. Conclusion

Thiol-acrylate click reaction was used to synthesize well-defined polymer networks containing both supramolecular UPy units and covalent crosslinks. This click chemistry allows precise tuning of the ratio between the transient supramolecular and permanent covalent crosslinks, covering the full range in the network topography. At a critical ratio, the network undergoes a transition from plasticity to elasticity. The experimental observations allow maximizing the contribution of supramolecular bonds in the network while keeping it in the elasticity region. This, coupled with the dynamic equilibrium nature of the UPy, leads to polymer networks with several unusual mechanical properties, including strong strain rate dependence, ultrasoft shape memory, and superior mechanical damping. Materials of such properties may enable new applications, which is the focus of our future study. In addition, other supramolecular bonds with different dynamic properties (e.g., timescale of the bond exchanges) are worth exploring as a way to tuning the dynamic macroscopic properties to meet various practical needs.

4. Experimental Section

Materials: *N*,*N*-Dimethylformamide (DMF) and triethylamine (TEA) were purchased from Aladdin. Pentaerythritol tetrakis (3-mercaptopropionate) (PTME) and poly(ethylene glycol) diacrylate (PEGDA) ($M_w \approx 700$ g mol^{-1}) were purchased from Sigma-Aldrich. Unless otherwise noted, all chemicals were used as received. UPy containing acrylate monomer (UPyA) was synthesized according to the literature.[8]

Polymer Network Synthesis: PTME and UPyA were added in DMF, followed by the addition of TEA (10 wt% of total monomer weight) as the catalyst. The resulting mixture was heated to 80 °C until UPyA was completely dissolved, after that PEGDA was added. The total monomer concentration was maintained at 30 wt% (by monomer weight) for these samples. The well stirred solution was injected between two glass slides (50 × 50 mm) separated by a silicon rubber spacer (1.2 mm thick) and the reaction proceeded in an oven at 80 °C for 6 h. The resulting gel was dried at 80 °C in vacuum until a constant weight was reached.

Shape Memory Tests: DMA experiments were conducted using DMA Q800 in a "control force" mode. Shape fixity and recovery were calculated by Equation (2)

$$R_f = \frac{\varepsilon_d}{\varepsilon_{dload}} \text{ and } R_f = \frac{\varepsilon_d - \varepsilon_{100}}{\varepsilon_d} \tag{2}$$

where ε_{dload} represents the maximum strain under load, ε_{rec} is the recovered strain, and ε_d is the fixed strain after cooling and load removal.

Tensile Testing: Tensile testing was performed on a universal material testing machine (Zwick/Roell Z005) equipped with a thermal chamber. Experiments were conducted at 25, 55, and 85 °C, at strain rates of 10, 100, 1000, and 10 000% min^{-1}. Five tests were run for each sample. Data for **UPy40** at 55 and 85 °C with a strain rate of 10% min^{-1} were measured using a DMA machine due to its softness.

Fabrication of Spherical Balls: Each ball was made by injecting the monomer solution into a hollow glass sphere mold. Solvent was evaporated after gelation and the ball was obtained after breaking the glass sphere.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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