Optically responsive supramolecular polymer glasses

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The reversible and dynamic nature of non-covalent interactions between the constituting building blocks renders many supramolecular polymers stimuli-responsive. This was previously exploited to create thermally and optically healable polymers, but it proved challenging to achieve high stiffness and good healability. Here we present a glass-forming supramolecular material that is based on a trifunctional low-molecular-weight monomer ((UPyU)₃TMP). Carrying three ureido-4-pyrimidinone (UPy) groups, (UPyU)₃TMP forms a dynamic supramolecular polymer network, whose properties are governed by its cross-linked architecture and the large content of the binding motif. This design promotes the formation of a disordered glass, which, in spite of the low molecular weight of the building block, displays typical polymeric behaviour. The material exhibits a high stiffness and offers excellent coating and adhesive properties. On account of reversible dissociation and the formation of a low-viscosity liquid upon irradiation with ultraviolet light, rapid optical healing as well as (de)bonding on demand is possible.
Supramolecular polymers are assembled from monomeric building blocks through non-covalent, directional interactions, such as H-bonding, π–π stacking and ligand–metal complexation. The nature and strength of useful supramolecular interactions vary widely. The reversible and in many cases dynamic nature of supramolecular binding can be used to impart a wide range of stimuli-responsive characteristics, including mechanochromism, bioactivity and mechanical morphing. The possibility to temporarily reduce the molecular weight of the supramolecular assemblies by shifting the equilibrium to the monomer side upon exposure to an appropriate stimulus can also be used to create healable (or self-healing, if the system is sufficiently dynamic under ambient conditions) polymers. This is the result of an increased chain mobility and decreased viscosity upon disassembly, which enable the material to flow and fill cracks and gaps before the original material is reformed by shifting the equilibrium back to the assembled state. The same approach can be used to create reversible adhesives that permit (de)bonding on demand. Examples of thermally healable materials based on this general concept include hydrogen-bonded rubbers based on telechelic poly(ethylene-co-butylene) functionalized with ureido-4-pyrimidinone (UPy) units, elastomer networks based on fatty acids, ethylene diamine and urea, and phase-separated elastomers based on a polystyrene-polyacrylic acid brush copolymer. Optically healable supramolecular polymers, which are advantageous because the stimulus can be applied in a targeted manner, have also been realized, for example, on the basis of telechelic poly(ethylene-co-butylene) that was chain-terminated with terdentate ligands and assembled into a polymer with stoichiometric amounts of Zn²⁺ or Eu³⁺ salts. However, on account of the dynamic nature of the supramolecular motifs employed, and the use of building blocks with low glass transition temperature (Tg), virtually all known healable supramolecular polymers exhibit a low resistance to mechanical stress. This problem can to a certain extent be overcome by the introduction of a reinforcing (nano)filler, but even with this improvement the stiffness (storage modulus of <250 MPa) and strength (tensile strength of <5 MPa) are rather low and stifle the exploitation of such materials as a replacement of glassy thermoset resins in coatings, adhesives and other applications. In this study, we show that the combination of high stiffness imparted by supramolecular moieties and stimuli-responsive behaviour is accessible with supramolecular polymer glasses based on a low-molecular-weight, tri-functional supramolecular monomer, which assembles into a disordered supramolecular network. Although molecular glasses represent a well-investigated class of materials, supramolecular polymer glasses based on small molecules have been rarely observed and remain hardly explored. Known examples of such materials show either a glass transition close to room temperature or the tendency to rapidly crystallize above the Tg. Here we report a supramolecular glass that exhibits a high Tg and a low tendency to crystallize upon cooling from the melt. The design principles used here appear to be general and should permit easy access to other representatives of this interesting class of materials.

Results

Design and synthesis of a supramolecular glass. The optically responsive supramolecular material studied here is based on a trifunctional low-molecular-weight monomer (UPy functionalized 1,1,1-tris(hydroxymethyl)propane ([(UPy)₃TMP]) that carries ureido-4-pyrimidinone (UPy) groups (Fig. 1a,b). The UPy motif, originally developed by Meijer and co-workers, and selected because it forms strong self-complementary hydrogen-bonded dimers, is easy to synthesize and its dynamic binding is well investigated. Much of the previous work on UPy-based supramolecular polymers has focused on telechelic monomers with two terminal binding motifs that promote linear chain extension, and macromolecular systems in which UPy side chains serve as reversible cross-links; these approaches afford...
supramolecular polymers whose properties are to a large extent
governed by the nature of the telechelic or polymeric building
blocks. By contrast, the trifunctional (UPyU)_3TMP introduced
here was designed to form a supramolecular network whose
properties are dictated by the cross-linked nature and the large
content of the binding motif. We further surmised that the high
concentration of the supramolecular motif, which tilts the dynamic
equilibrium towards the bound state (Fig. 1a), and the cross-linked
nature, which reduces the molecular mobility of the monomers,
would hamper crystallization and permit kinetic trapping of a
disordered amorphous glass upon cooling the material from a
dissociated melted state. Finally, we have shown recently that,
if used in a sufficiently high concentration, the UPy motif can
serve as an efficient light-heat converter and can be used to
bestow polymers with optical responsiveness to permit features
such as optical healing and (de)bonding on demand.

(UPyU)_3TMP was prepared by reacting 1,1,1-tris
(hydroxymethyl)propane with three equivalents of 2-(6-isocya-
natohexylaminocarbonylamino)-6-methyl-4[1H]pyrimidinone
using isocyanate chemistry (Fig. 1b). This simple reaction, which
was carried out in hot pyridine to prevent network formation
during the reaction and co-crystallization of solvent, as was
observed when dimethylformamide was employed, afforded the
new monomer in good yield. Precipitation of the product from
the reaction mixture upon cooling afforded the product as
analytically pure semi-crystalline powder, which upon melting
turned into a clear, glassy material (Fig. 1c).

Properties of (UPyU)_3TMP. Thermogravimetric analysis (TGA)
and differential scanning calorimetry (DSC) were used to
determine the thermal properties of (UPyU)_3TMP. The TGA of
the as-prepared material (Supplementary Fig. 1) shows a 2%
weight loss at 246°C; above this temperature the decomposition
rate accelerates. The DSC first heating trace of the as-prepared
monomer shows a weak endothermic transition at 80°C, which
is associated with the glass transition, and an endothermic peak
at 178°C, corresponding to melting of the crystalline portion
(Fig. 2a). The cooling scan reveals a glass transition around
100°C and is void of any other transitions, even at a cooling rate
as low as 1°C min⁻¹ (Supplementary Fig. 2), demonstrating that
upon melting and cooling, (UPyU)_3TMP forms a completely
amorphous solid. This is confirmed by the second DSC
heating trace, which also only shows a glass transition at 106°C.
Moreover, the DSC traces of (UPyU)_3TMP glasses that were kept
at ambient temperature for up to 7 months did not show any
signs of crystallization upon storage (Supplementary Fig. 3).
The interpretation of the DSC experiments was confirmed by
powder X-ray diffraction experiments. The diffractogram of the
as-prepared (UPyU)_3TMP shows a superposition of an amor-
phous halo and well-defined reflections, whereas the diffrac-
togram of a sample that had been heated to 200°C and cooled
to 125°C showed a small hysteresis (Fig. 2b). The broad
amorphous broadening indicated by the DSC is confirmed by
the high stiffness. Three-point bending tests conducted at the
same temperature confirmed the high stiffness (flexural
modulus = 3.04 ± 0.26 GPa) and revealed a strain at break of
0.26 ± 0.03% (Fig. 3b and Table 1) and a stress at break of
6.42 ± 0.20 MPa. These data reflect that (UPyU)_3TMP is quite
brittle. We further probed the mechanical properties of the
surface of a ca. 300-µm-thin (UPyU)_3TMP film that had been
melt-deposited on a glass substrate by depth-sensing indentation
and atomic force microscopy (AFM) in force spectroscopy mode,
in the latter case also as function of temperature. The room
temperature Young’s moduli—3.7 ± 0.1 GPa measured by inden-
tation (Supplementary Fig. 5) and 2.7 ± 0.1 GPa measured by
AFM (Fig. 3c)—are comparable to the value determined by DMA.
Temperature-dependent AFM data reveal a significant modulus
decrease upon heating, with an onset around 105°C (Fig. 3c). A
comparison with the DSC and DMA data makes evident that this
stiffness decrease is associated with the transition from the glassy

Figure 2 | Thermal properties and morphology of (UPyU)_3TMP. (a) Differential scanning calorimetry (DSC) traces (first heating (—), first
cooling (— - -) and second heating (····) of the as-prepared material. The experiment was conducted with heating and cooling rates of 10°C min⁻¹
under N₂ atmosphere; traces with other heating and cooling rates are
provided as Supplementary Information. (b) Powder X-ray diffraction diagrams
for the as-prepared (top) material and a sample that had been heated to
200°C and cooled to ambient.

Figure 3 | Properties of (UPyU)_3TMP. Thermogravimetric analysis (TGA)
and differential scanning calorimetry (DSC) were used to
determine the thermal properties of (UPyU)_3TMP. The TGA of
the as-prepared material (Supplementary Fig. 1) shows a 2%
weight loss at 246°C; above this temperature the decomposition
rate accelerates. The DSC first heating trace of the as-prepared
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upon melting and cooling, (UPyU)_3TMP forms a completely
amorphous solid. This is confirmed by the second DSC
heating trace, which also only shows a glass transition at 106°C.
Moreover, the DSC traces of (UPyU)_3TMP glasses that were kept
at ambient temperature for up to 7 months did not show any
signs of crystallization upon storage (Supplementary Fig. 3).
The interpretation of the DSC experiments was confirmed by
powder X-ray diffraction experiments. The diffractogram of the
as-prepared (UPyU)_3TMP shows a superposition of an amor-
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Temperature-dependent AFM data reveal a significant modulus
decrease upon heating, with an onset around 105°C (Fig. 3c). A
comparison with the DSC and DMA data makes evident that this
stiffness decrease is associated with the transition from the glassy
is the heat flow determined by DSC (second heating recorded at a rate of 10 °C/min) and is shown to be viscoelastic properties. Further, a significant decrease of the storage modulus (G’) of (UPyU)3TMP; shown are storage modulus (G’) and loss modulus (G”) as a function of temperature with temperature dependence of the storage (G’) and loss (G”) moduli between 150 and 200 °C (Supplementary Fig. 7), suggesting polymer-like behavior of these glasses (Supplementary Fig. 8). DSC experiments show that the (UPyU)3TMP supramolecular glass is heated above Tg (Supplementary Fig. 6). The mechanical properties of (UPyU)3TMP are largely a result of the high cross-link density of the material in the solid state as well as above Tg. We surmised that the introduction of a UPy-functionalized chain stopper would decrease the cross-link density and therefore influence the properties. To test this hypothesis, a mono-functional UPy-containing molecule was synthesized (2(6-(2-ethylhexyl)-8-hexylurea-aminocarbonylamino)-6-methyl-4H-pyrimidinone (UPy-C6-U-EH), Fig. 4a) and melt-mixed in various ratios with (UPyU)3TMP to form a series of amorphous supramolecular glasses (Supplementary Fig. 8). DSC experiments show that the Tg of these glasses decreases with increasing content of UPy-C6-U-EH (Fig. 4b and Supplementary Fig. 9).

Table 1 | Mechanical properties of (UPyU)3TMP and (UPyU)3TMP(UPy-C6-U-EH)0.33

| Sample                        | Storage modulus (GPa) | Flexural modulus (GPa) | Flexural stress at break (MPa) | Flexural strain at break (%) |
|-------------------------------|-----------------------|------------------------|-------------------------------|-------------------------------|
| (UPyU)3TMP                   | 3.65 ± 0.51           | 3.04 ± 0.26            | 6.42 ± 0.20                   | 0.26 ± 0.03                   |
| (UPyU)3TMP(UPy-C6-U-EH)0.33  | 2.87 ± 0.36           | 2.08 ± 0.28            | 5.61 ± 0.96                   | 0.30 ± 0.03                   |
| (UPyU)3TMP(UPy-C6-U-EH)0.1   | 2.21 ± 0.77           | 1.68 ± 0.14            | 4.53 ± 0.95                   | 0.33 ± 0.09                   |
| (UPyU)3TMP(UPy-C6-U-EH)0.005 | 1.47 ± 0.29           | 1.29 ± 0.12            | 4.44 ± 0.83                   | 0.34 ± 0.06                   |
| (UPyU)3TMP healed0.5         | NA                    | 2.80 ± 0.43            | 4.81 ± 2.74                   | 0.27 ± 0.15                   |

Abbreviation: NA, not applicable; UPy, ureido-4-pyrimidinone; (UPyU)3TMP, UPy-functionalized 1,1,1-tris(hydroxymethyl)propane; UPy-C6-U-EH, 2(6-(2-ethylhexyl)-8-hexylurea-aminocarbonylamino)-6-methyl-4H-pyrimidinone.

1Measured by DMA at 25 °C with n = 3 individual measurements.
2Measured by three-point bending stress–strain experiments at 25 °C, n = 5 (except for healed samples, where n = 10).
3Samples were cut in half, partly overlapped and irradiated with ultraviolet light (320–390 nm, 650 mW/cm², 2 x 12 s).

into a rubbery state. AFM force spectroscopy measurements also reveal a significant increase in adhesion above the Tg (Supplementary Fig. 6). The AFM data permit the conclusion that the UPy–UPy interactions are not simply ‘switched off’ when the (UPyU)3TMP supramolecular glass is heated above Tg; instead, a dynamic equilibrium between bound and dissociated states exists, which is shifted to the monomer side as the temperature is increased. Rheological studies were conducted to confirm this interpretation, which is consistent with the results of previous studies in which UPy dimerization was investigated as a function of temperature14. Frequency sweep experiments performed in the linear viscoelastic regime show a frequency dependence of the storage (G’) and loss (G”) moduli between 150 and 200 °C (Supplementary Fig. 7), suggesting polymer-like viscoelastic properties. Further, a significant decrease of the G’ and G” was observed upon heating the material (Fig. 3d), suggesting a reduction of the virtual molecular weight on account of reducing the cross-link density by shifting the dynamic equilibrium towards the dissociated state.

The mechanical properties of (UPyU)3TMP are largely a result of the high cross-link density of the material in the solid state as well as above Tg. We surmised that the introduction of a UPy-functionalized chain stopper would decrease the cross-link density and therefore influence the properties. To test this hypothesis, a mono-functional UPy-containing molecule was synthesized (2(6-(2-ethylhexyl)-8-hexylurea-aminocarbonylamino)-6-methyl-4H-pyrimidinone (UPy-C6-U-EH), Fig. 4a) and melt-mixed in various ratios with (UPyU)3TMP to form a series of amorphous supramolecular glasses (Supplementary Fig. 8). DSC experiments show that the Tg of these glasses decreases with increasing content of UPy-C6-U-EH (Fig. 4b and Supplementary Fig. 9).
temperature. All samples were prepared by melt mixing (UPyU)3TMP with UPy-C6-U-EH at 200°C. Differential scanning calorimetry (DSC) traces show an absorption band below 350 nm that can be attributed to the UPy motif (Fig. 5b). When the bonded lap joints were placed under load and exposed to ultraviolet light, healing was also possible on glass (which has a higher thermal conductivity than wood), even when the power density was reduced to 250 mW cm⁻². AFM images (Fig. 6c) show that a ca 10-µm-wide cut vanishes after 12 s of ultraviolet exposure, although a very shallow scar remained (Fig. 6c and Supplementary Fig. 12). AFM force spectroscopy confirmed that the original and healed samples are identical in regard to their mechanical behaviour (Supplementary Fig. 13). The high optical absorption imparted by the high UPy content (Fig. 5b), and the capability to dissociate into a low-viscosity melt should bestow the supramolecular (UPyU)3TMP glass with excellent optical healing capabilities. To test this, a piece of wood was coated with a 300-µm-thin layer of amorphous (UPyU)3TMP and the coating was intentionally damaged by cutting with a razor blade (Fig. 6a). The damaged area was subsequently exposed to ultraviolet irradiation (320–390 nm, 500 mW cm⁻²), which led to disappearance of the cut in as little as 12 s (Fig. 6a and Supplementary Movie 3). We monitored the temperature increase of the material with the help of an infrared thermometer; the data show a rapid and localized temperature increase to 188°C (Fig. 6b). AFM images (Fig. 6c) show that a ca 10-µm-wide cut vanishes after 12 s of ultraviolet exposure, although a very shallow scar remained (Fig. 6c and Supplementary Fig. 12), whereas AFM force spectroscopy confirmed that the original and healed samples are identical in regard to their mechanical behaviour (Supplementary Fig. 13). The high transparency of (UPyU)3TMP also allowed optical welding of two films that were overlapped by irradiating such an assembly (320–390 nm, 650 mW cm⁻², 2 × 12 s, Fig. 6d). The results of the three-point bending tests show no statistically significant difference from the original samples (Fig. 6e and Table 1) and samples were observed to always break outside of the mended area. We note that the healing and welding time depends on the light intensity and thermal conductivity of the substrate, which serves as a heat sink. Healing was also possible on glass (which has a higher thermal conductivity than wood), even when the power density was reduced to 250 mW cm⁻² (Supplementary Fig. 14).

Figure 4 | Influence of the addition of a chain stopper on the properties of (UPyU)3TMP. (a) Molecular structure of the chain stopper UPy-C6-U-EH. (b) Representative dynamic mechanical analysis (DMA) traces. (c) Elastic modulus as function of temperature. All samples were prepared by melt mixing (UPyU)3TMP with UPy-C6-U-EH at 200°C and cooling to ambient.
Characterization. $^1$H (360 MHz) and $^{13}$C (90 MHz) NMR spectra were recorded on a Bruker Avance III spectrometer in dimethylsulfoxide (DMSO)-d$_6$. $^1$H NMR coupling constants are given in Hz. $^1$H NMR spectra were referenced against the signal of residual DMSO at 2.50 p.p.m. and $^{13}$C NMR spectra were referenced against the DMSO-d$_6$ signal at 39.52 p.p.m. TGAs were conducted under $N_2$ using a Mettler-Toledo STAR thermogravimetric analyser in the range of 25–500 °C with a heating rate of 10 °C min$^{-1}$. DSC measurements were performed under a Mettler-Toledo STAR system operating at a heating/cooling rate of 5 °C min$^{-1}$ in the range −70 to 150 °C, unless indicated otherwise. Data from the second heating cycle and the reverse heat flow curve are reported unless indicated otherwise (T$_g$ = glass transition temperature). DMA$\_s$ were performed on a TA Instruments DMA Q800 with a heating rate of 5 °C min$^{-1}$ and a frequency of 1 Hz in the range of −50 to 140 °C using a three-point bending setup. Three-point bending tests were conducted on the same instrument at 25 °C, with a displacement rate of 100 μm min$^{-1}$. All mechanical tests were conducted on rectangular samples (typical dimensions: 25 mm × 5 mm × 230 μm). Flexural moduli were determined from the curves, as all samples displayed a linear relationship between stress and strain until failure. Load-sensing indentation measurements were performed using a CSM Ultra Nanoindenter equipped with a Berkovich tip (diamond). All experiments were performed using a loading and unloading rate of 100 μN min$^{-1}$ and 15 min of constant load (100 μN) before unloading to allow for creep deformation. AFM images and force spectroscopy measurements were performed on a JPK Nano Wizard II. AFM images were recorded with NanoWorld NCHR high-resolution frequency tips. Force spectroscopy tests were performed with a Bruker DNISP cantilever with a cube corner diamond tip (nominal sensitivity = 249 N m$^{-1}$). Temperature-dependent AFM force spectroscopy tests were performed on thin res with a thickness of 300 μm on a microscopy glass slide and placed on a JPK HTHS high-temperature heating stage, and the sample surface temperature was continuously monitored using a hand-held infrared camera. All recorded unloading curves were fitted (upper 50% of the unloading curve) and analysed according to the Oliver and Pharr model to yield the elastic modulus, assuming a Poisson ratio of 0.3 and a perfect cube clasper tip. Rheological studies were performed on a TA instruments ARG2 Rheometer operating with a Pellet heating stage and parallel plate geometry. Ultraviolet−visible absorption spectra were measured on a Jasco V-670 spectrophotometer. Electrospray ionization mass spectrometry (ESI-MS) was measured by the Laboratory for Mass Spectroscopy of the University of Fribourg. Elemental analysis was performed by the Service d’analyses chimiques de l’Ecole d’ingénieurs et d’architectes de Fribourg. FT-IR spectra were measured on a Perkin-Elmer Spectrum 65 spectrometer using dried (crystalline powder in attenuated total reflection (ATR) mode between 800 and 4000 cm$^{-1}$ with five accumulated scans per sample. Ultraviolet irradiation of the samples to achieve healing was performed with a Hoezel Blueprint 4 Ecourve lamp connected to an optical fibre. An optical filter was used to irradiate limit the output to the wavelength range of 320–390 nm. The temperature increase during ultraviolet irradiation was monitored using an Opitres PI connect infrared camera. Adhesion tests were performed by adhering two regular glass slides (overlapping area = 10 × 25.7 mm$^2$) with a thin layer of (UPyU)$_2$TMP. The adhesive properties were determined with a Zwick/Roell Z101 tensile tester at room temperature with a strain rate of 0.1 mm min$^{-1}$. Synthetic methods. Synthesis of (UPyU)$_2$TMP. For the synthesis of (UPyU)$_2$TMP, a round bottom flask equipped with a reflux cooler was charged with 1,1,1-tris(hydroxymethyl)propane (635 mg, 4.7 mmol), 2-(6-isocyanatoethylaminocarbamoyl)aminocarboxylic acid (5.0 g, 17 mmol), dibutyltin dilaurate (60 μL, ~3 mol%) and dry pyridine (300 mL) under an N$_2$ atmosphere. The reaction mixture was heated to reflux temperature (120 °C) and was stirred for 20 min to achieve complete dissolution of the UPy isocyanate. DMSO was added to the reaction mixture in the range of 25–500 °C and solids were removed from the reaction mixture by vacuum filtration. The filtrate was cooled to room temperature and a white precipitate was observed. Acetone (200 mL) was added to the filtrate, and the solids were collected by filtration. The precipitate was washed with acetone (3 × 100 mL) and dried in vacuo at 70 °C for 12 h to yield the analytically pure product as white crystalline powder (3.7 g, 3.6 mmol, 53%). We note that the product has poor solubility in common solvents, and all NMR samples were prepared by heating to 100 °C in DMSO-d$_6$ for 20 min to achieve complete dissolution (c = 2 mg mL$^{-1}$). Cooling to room temperature resulted in solutions that were stable for up to 2 h. $^{1}$H NMR (DMSO-d$_6$, 360 MHz) $\delta$ = 11.53 (s, 3H), 9.67 (s, 3H), 7.39 (s, 3H), 7.09 (s, 3H), 2.93 (s, 6H), 3.85 (t, 6H), 3.12 (t, 6H), 2.10 (s, 9H), 1.43–1.27 (m, 26H), 0.8 (s, 3H). $^{13}$C NMR (CDCl$_3$, 91 MHz) $\delta$ = 173.67, 158.98, 156.99, 155.13, 148.73, 147.08, 107.05, 103.68, 41.11, 40.10, 36.59, 30.56, 29.85, 26.75, 19.35. ESI-MS: $m/z$ calculated: 1014.1; found: 1014.2. Analysis calculated for C$_{45}$H$_{71}$N$_{15}$O$_{12}$: C = 53.29, H = 7.06, N = 20.72. Found: C = 53.30, H = 7.46, N = 20.80. Synthesis of UPy-C6-U-EH. For the synthesis of UPy-C6-U-EH, a round bottom flask was charged with 2-ethylhexyl-1-amine (559 μL, 3.4 mmol), aminocarbonylaminocarbamoyl(aminocarbonylaminocarbamoyl)-6-methyl-4[H]pyrimidinone was synthesized as previously reported.$^{34,35}$
Figure 6 | Optical healing of the (UPyU)₃TMP supramolecular glass. (a) Pictures showing the optical healing of a damaged coating on wood. The 300-μm-thin coating was cut with a razor blade (top) and subsequently exposed to ultraviolet light for 12 s, which caused complete healing (bottom). (b) Surface temperature measured using an infrared camera upon irradiating the coating with ultraviolet light. (c) AFM images of damaged (top) and healed coating exposed to ultraviolet light for 12 s (bottom). (d) Picture of welded (UPyU)₃TMP films; a film sample was cut in half, overlapped and irradiated with ultraviolet light (2 × 12 s). (e) Representative flexural stress-strain curve of a film mended as in (c) at 25 °C. An ultraviolet light source emitting at 320–390 nm and having a power density of 500 mW cm⁻² (for experiments in a,b,d) or 650 mW cm⁻² (for experiments in c,e) was used.

2-(6-isocyanatohexylaminocarbonylamino)-6-methyl-[1H]pyrimidinone (1.0 g, 3.4 mmol) and dry DMF (25 ml) under an N₂ atmosphere. The reaction mixture was heated to 90 °C for 12 h, and subsequently cooled to room temperature. The mixture was diluted with diethyl ether (100 ml), and a white precipitate was formed. The precipitate was filtered, washed with diethyl ether (2 × 50 ml) and dried in vacuo at 50 °C for 12 h to yield the pure product as white crystalline powder (1.3 g, 3.1 mmol, 90%). ¹H NMR (DMSO-d₆, 360 MHz) δ = 11.56 (s, 1H), 9.66 (s, 1H), 7.34 (s, 1H), 5.77 (s, 1H), 5.71 (q, 2H), 3.13 (q, 2H), 2.95 (dq, 4H), 2.10 (s, 3H), 1.44–1.25 (bm, 17H), 0.81 (dt, 6H). ¹³C NMR (101 MHz, DMSO) δ = 158.67, 142.32, 30.88, 30.48, 29.58, 28.89, 26.48, 26.45, 24.10, 23.01, 14.44, 11.27. ESI-MS: m/z: calculated: 422.3; found: 423.3 [M + 1]⁺.

General methods. Preparation of thin coatings and self-standing films. As-prepared (UPyU)₃TMP was heated in a microscopy glass for 5 min at 200 °C to yield a clear viscous material. The material was transferred with a spatula onto a preheated glass slide and doctor-bladed to form a homogenous film. To form a coating on wood, the viscous liquid material was placed on a hot microscopy glass slide and doctor-bladed onto the wood surface to achieve a homogenous coating. This process was repeated to yield a coating of around 300 μm thickness. Self-standing films were prepared by first heating the (UPyU)₃TMP powder to 200 °C in a vial and cooling the resulting viscous liquid to room temperature. The resulting amorphous material was compression molded in a Carver press between two Kapton sheets that were separated by Teflon spacers (145 μm-thin coating was cut with a razor blade. To minimize the influence of environmental conditions, mechanical tests were conducted within a day after producing the samples. Indentation measurements. For indentation measurements, a glassy (UPyU)₃TMP coating with a thickness of around 300 μm on a thin round glass substrate was prepared by melt deposition at 200 °C onto a thin glass substrate. The coating thickness was chosen with respect to Buckle’s one-tenth law to avoid any influence of the substrates on the measurement²⁰, and maximum indentation depths did not exceed 3 μm (<1%). Furthermore, as a control experiment to improve the reliability of the fitted data, AFM images of indents (for indentation forces of 150 and 300 μN) were acquired. Perfect cube corner indents with only limited pile-up (Supplementary Fig. 15) are seen, especially for indents with a force of 150 μN, which was used for all AFM force spectroscopy experiments. We note that fitted data from nano indentation measurements yield a comparative impression of the order magnitude of stiffness, and do not give absolute values for the stiffness. Depth-sensing indentation measurements were performed by indentation at room temperature with a maximum force of 100 μN at a loading and unloading rate of 100 μN min⁻¹. Before each measurement, a height calibration of the local sample surface was performed. Unloading curves were used to determine the elastic modulus according to the Oliver and Pharr model using CSM.
nanoindentation software. AFM force spectroscopy measurements were carried out by using a cube corner diamond tip cantilever. An indentation force of 150 μN was chosen to respect the indentation depth limitation dictated by Buckle's Law regarding effects of the substrate. Data were then analysed using the Oliver and Pharr model with a Poisson ratio of 0.3 and the slope of the initial part (that is, upper 50%) of the unloading indentation curve. Rheology. All rheological studies were carried out using parallel plate geometry and controlled normal force (between −0.5 and 0.5 N). Samples were measured by heating (UPyU)3TMP or mixtures of (UPyU)3TMP and (UPy-C6-U-EH) to 200 °C for 2 min before the rotating parallel plate was lowered until the material was observed to flow out on all sides of the upper plate; subsequently, excess material was removed to prevent edge effects on the data. Frequency sweep experiments were conducted at fixed temperature intervals between 200 and 90 °C at a strain of 0.2% and a frequency of 20 rad s⁻¹. The data were analysed with TA instruments software, and further processed with graphing software. Data were rejected when the strain on the sample was <75% of the strain applied.

Chains stopper experiment. (UPyU)3TMP and varying amounts of UPy-C6-U (0.33, 1.0 and 1.5 molecular equivalents) were mixed as powders and then heated to 200 °C for 15 min to yield a clear homogeneous melt. Coatings and films for AFM force spectroscopy measurements, DMA and three-point bending tests were prepared as described above for the neat (UPyU)3TMP.

Adhesive properties and optical debonding. The adhesive properties of (UPyU)3TMP on robust glass substrates were determined with a tensile tester at room temperature with a strain rate of 0.1 mm min⁻¹. To do that, two glass slides were joined by a 30-μm-thick layer of (UPyU)3TMP at 200 °C and subsequent cooling to room temperature. For optical debonding experiments, glass slides (thickness = 140 μm) were joined together with (UPyU)3TMP in the same manner, and one side of the resulting lap joint was mounted into a holder, whereas a weight of 500 g was attached to the glass slide. Debonding was achieved by irradiation with ultraviolet light (320–390 nm, 1,000 mW cm⁻²). This experiment was conducted with thin glass slides to limit heat dissipation. Optical healing of scratches was performed on coatings of (UPyU)3TMP (thickness = 300 μm) that were damaged with a razor blade. Healing was achieved by irradiation with ultraviolet light (320–390 nm, 500 mW cm⁻², 12 s) and the temperature was monitored by an infrared camera. After 12 s, a small scar is still visible, and can be completely removed by another 12 s irradiation with the same intensity. For optical mending rectangular pieces of (UPyU)3TMP films were cut into two with a razor blade. The samples were overlapped and without external pressure irradiated with ultraviolet light (320–390 nm, 650 mW cm⁻², 2 × 12 s with 5 min between the exposures to allow for cooling to room temperature).

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Author contributions
C.W., G.L.F. and D.W.R.B. developed the original concept for the study and designed the materials and experiments. D.W.R.B. synthesized and characterized all materials and performed the experiments. C.A.M. carried out and interpreted the AFM indentation and imaging experiments. All authors discussed the results and contributed to the interpretation of data. C.W. and D.W.R.B. wrote the paper. All authors contributed to editing the manuscript.

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Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

Competing financial interests: The Adolphe Merkle Institute has filed a patent application related to healable supramolecular polymers with high stiffness, which lists some of the authors as inventors (C.W., D.W.R.B., G.L.F.).
