

Light-Induced Bonding and Debonding with Supramolecular Adhesives

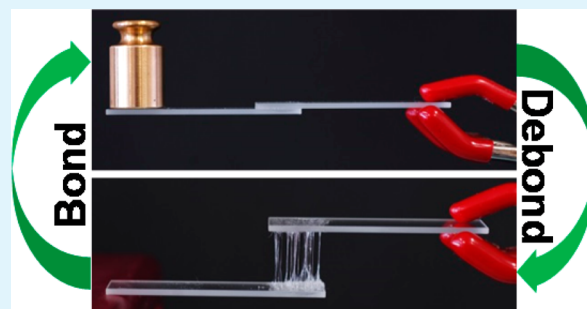
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S Supporting Information

ABSTRACT: Light-responsive supramolecular polymers were applied as reversible adhesives that permit bonding and debonding on demand features. A telechelic poly(ethylene-*co*-butylene) (PEB) was functionalized with either self-complementary hydrogen-bonding ureidopyrimidinone (UPy) motifs (UPy-PEB-UPy) or 2,6-bis(1'-methylbenzimidazolyl)-pyridine (Mebip) ligands (Mebip-PEB-Mebip), which can coordinate to metal ions (Zn(NTf₂)₂) and form a metallosupramolecular polymer with the sum formula [Zn_x(Mebip-PEB-Mebip)](NTf₂)_{2x}, with $x \approx 1$. In the latter case, light-heat conversion is facilitated by the ultraviolet (UV) light-absorbing metal-ligand motifs, while in the case of UPy-PEB-UPy a UV absorber was added for this purpose. Single lap joints were prepared by sandwiching films of the supramolecular polymers of a thickness of 80–100 μm between two glass, quartz, or stainless steel substrates and bonded by exposure to either UV light (320–390 nm, 900 mW/cm²) or heat (80 or 200 °C for UPy-PEB-UPy and the metallopolymer, respectively). UPy-PEB-UPy and [Zn_{0.8}Mebip-PEB-Mebip](NTf₂)_{1.6} displayed a shear strength of 0.9–1.2 and 1.8–2.5 MPa, respectively. When lap joints were placed under load and exposed to light or heat, the samples debonded within seconds. They could be rebonded through exposure to light or heat, and the original adhesive properties were recovered.

KEYWORDS: reversible adhesive, light-triggered, noncovalent interactions, stimuli-responsive, supramolecular polymer, bonding and debonding on demand



INTRODUCTION

Adhesives with switchable properties allow for the formation of reversibly bonded joints and can thus offer bonding and debonding on demand capabilities.^{1–8} This feature has been met with significant interest in different fields of materials science and engineering and is useful for countless applications, including the disassembly of bonded components in automated production processes,^{3,7} the repair of complex structural components in bonded parts,^{9–12} the painless removal of wound dressings,^{13–17} or the simplification of materials separation to aid recycling of goods at the end of their lifespan.^{9,10,18–20} Hot-melt adhesives represent the simplest and most commonly used type of reversible adhesives, but a plethora of other design concepts have been developed to impart debonding on demand (DOD) capabilities to a broad range of adhesives, including heat-expandable fillers, as well as thermal or catalytic degradation.^{2–5,21} As an alternative to adhesives which can be bonded and debonded at elevated temperature, several other stimuli-responsive polymers were also used for DOD applications, for example pH-, pressure-, and light-responsive materials.^{22–25} A particularly intriguing approach is the use of supramolecular polymers, which are assembled with the help of noncovalent binding motifs.^{26–34}

This design permits the temporary disassembly of the polymer upon exposure to an appropriate stimulus.^{35–38} The

resulting decrease in the material's viscosity can significantly influence its adhesive properties, whereas the original material is reformed when the stimulus is removed and the equilibrium shifts back to the assembled state. This responsiveness has been exploited in a telechelic poly(ethylene-*co*-butylene) functionalized with hydrogen-bonding ureidopyrimidinone (UPy) groups at the termini (UPy-PEB-UPy, Figure 1).³⁹ Freshly cut pieces of this material heal autonomously when pressed together,²⁹ and patent literature reports that objects can be bonded/debonded with this material when heat is applied.⁴⁰ Our research group studied metallosupramolecular polymers in which defects can be healed upon exposure to ultraviolet (UV) light^{41–43} and similar materials were since demonstrated to be thermally healable.⁴⁴ These materials feature macromonomers that are also based on a telechelic poly(ethylene-*co*-butylene), but are terminated with 2,6-bis(1'-methylbenzimidazolyl)-pyridine (Mebip) ligands (Mebip-PEB-Mebip) (Figure 1). These building blocks can be assembled into polymeric structures with approximately stoichiometric amounts of Zn²⁺ and La³⁺ salts. The metal-ligand motifs absorb incident UV light and convert it into heat, which causes the temporary

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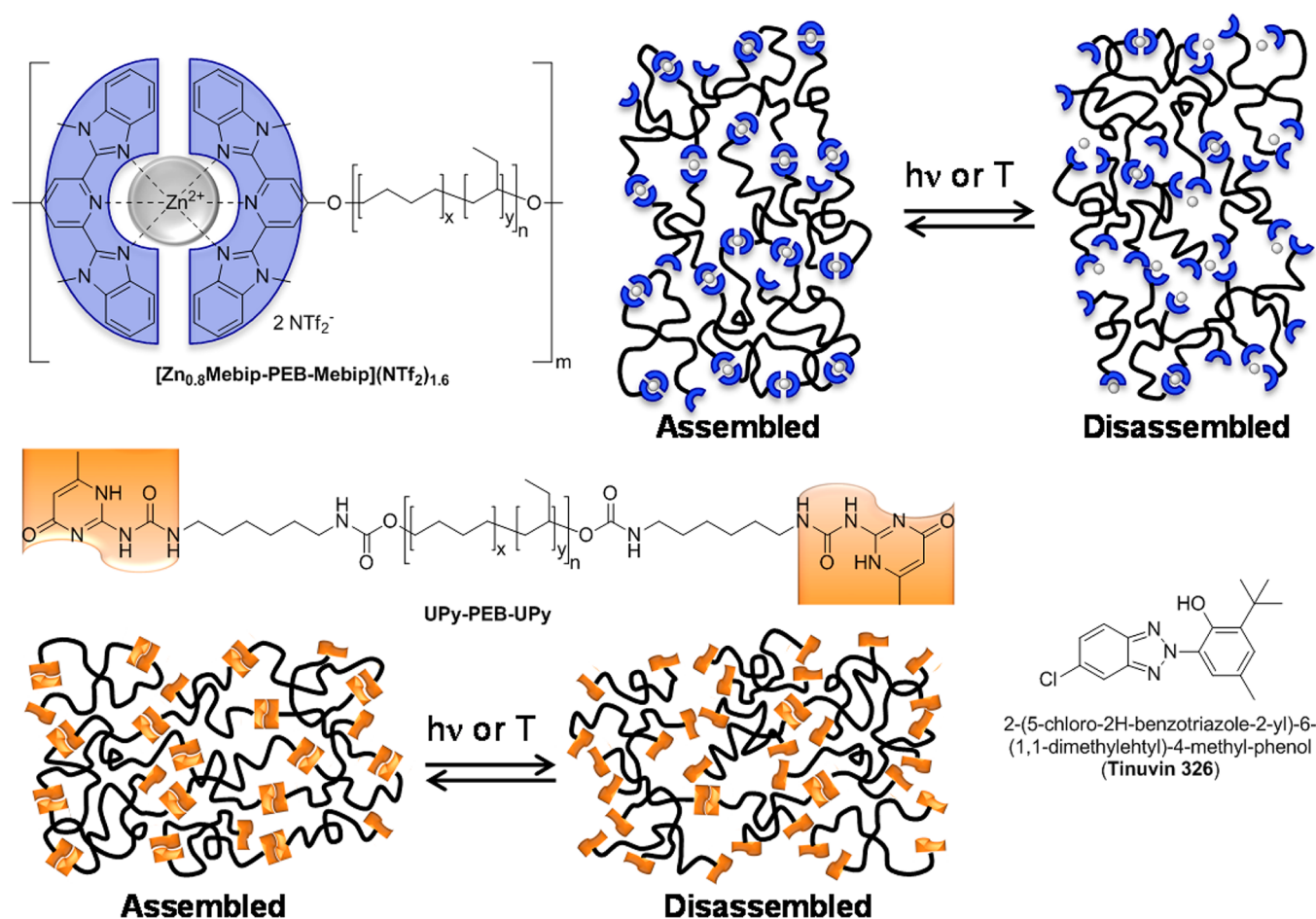


Figure 1. Chemical structures for the components of the $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ and UPy-PEB-UPy supramolecular polymers, and the UV absorber (Tinuvin 326). Also shown are schematic representations of the stimuli-responsive assembly and disassembly of supramolecular polymers using light or heat.

dissociation of the metal-ligand motifs and transforms the material into a low-viscosity liquid. When the light is switched off, the metallopolymers re-assemble and their original properties are restored. A similar behavior was reported for nanocomposites consisting of either Mebip-PEB-Mebip-based metallopolymers⁴³ or UPy-PEB-UPy⁴⁵ as the matrix and cellulose nanocrystals as a filler. These studies showed that the mechanical properties of the supramolecular polymers can be tailored by introduction of cellulose nanocrystals, which can cause an increase in stiffness of more than two orders of magnitude. The use of light to temporarily disassemble these supramolecular polymers and nanocomposites is attractive, because this stimulus can be applied locally and often more readily than other stimuli, for example in places that are difficult to access,⁴⁶ in situations where heat transfer is inadequate,^{46,47} or where the application of other stimuli could be harmful to the environment, such as in biomedical applications.⁴⁸ Obviously, however, this approach can only be used if the site permits access to UV light. Although examples of adhesives that allow for bonding and debonding upon exposure to light are generally rare,^{24,49,50} and examples of optically healable polymers are emerging,⁴² there are, to our best knowledge, no reports on light-triggered (de)bonding on demand scenarios with supramolecular polymers. Building on previous studies that have detailed the stimuli-induced (dis)assembly of these supramolecular polymers,^{26,27,31,34,35,37,39,41–45} we report that

this is readily feasible with adhesives based on sensitized UPy-PEB-UPy and Mebip-PEB-Mebip.

EXPERIMENTAL SECTION

Materials. UPy-PEB-UPy and Mebip-PEB-Mebip were synthesized from hydroxyl-terminated poly(ethylene-co-butylene) ($M_n = 3100$ g/mol; polydispersity index = 1.05), donated by Cray Valley SA (Krasol HLBH-P 3000), as previously reported^{39,41} and characterized to satisfaction by NMR, IR, and GPC (Supporting Information). In the case of the metallopolymers, 0.8 eq. of $\text{Zn}(\text{NTf}_2)_2$ was used per mole of Mebip-PEB-Mebip, affording metallosupramolecular polymers with the sum formula $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$. Acidic impurities were removed from spectroscopic grade CHCl_3 by passage through a plug of dry, activated (Brockman I) basic alumina prior to use. Tetrahydrofuran was purified by passage through alumina columns. Anhydrous CH_3CN (Sigma-Aldrich), chelidamic acid (Intatrade Chemicals GmbH), and all other solvents and reagents were used as received.

Methods. ¹H (300 MHz) and ¹³C (75 MHz) NMR spectra were recorded on a Bruker Advance III spectrometer in CDCl_3 unless indicated otherwise. Resonances are referenced against the signal of residual CHCl_3 at 7.260 ppm. ¹H NMR coupling constants are given in hertz. UV-Vis spectra were recorded on a Shimadzu UV-2401 PC spectrophotometer in $\text{CHCl}_3/\text{CH}_3\text{CN}$ (9:1 v/v) or CHCl_3 solution, or as thin films that were drop-cast from CHCl_3 onto quartz slides. Molecular weights were determined by gel permeation chromatography (GPC) (THF, 40 °C, 1.0 mL/min) using multi-angle laser light scattering (MALLS) ($\lambda = 658$ nm, 25 °C) and refractive index ($\lambda = 658$ nm, 40 °C) detection. A Varian 5 μm mixed-C guard column and

two GPC columns along with Wyatt Technology Corp. (Optilab REX interferometric refractometer, miniDawn TREOS laser photometer) and Agilent Technologies instrumentation (series 1200 HPLC) and Wyatt Technology software (ASTRA) were used for GPC. The incremental refractive index (dn/dc) was estimated by a single-injection method that assumed 100% mass recovery from the columns. Thermogravimetric analyses (TGA) were conducted under N_2 using a Mettler-Toledo Star[®] system thermogravimetric analyzer in the range of 25 °C to 600 °C with a heating rate of 10 °C/min. Polymer films were produced by compression molding with a Carver[®] CE Press under elevated temperatures (80 °C, 3 tons of pressure, 5 min for UPy-PEB-UPy; 200 °C, 5 tons of pressure, 5 min for $[Zn_{0.8}Mebip-PEB-Mebip](NTf_2)_{1.6}$) and using spacers of either 80 μm thickness for adhesive experiments or 180 μm for DMTA and stress-strain measurements. It is noted that films with different thickness were used to optimally meet the requirements of the respective measurement techniques.⁵¹

Dynamic mechanical thermal analyses (DMTA) were conducted under N_2 on a TA Instruments DMA Q 800 with a heating rate of 3 °C/min, a frequency of 1 Hz, and an amplitude of 15 μm in the range of -70 °C to 250 °C, unless indicated otherwise. The stress-strain measurements were conducted at 25 °C, with a strain rate of 5%/min with dog-bone-shaped samples (cross-section: 2.1 \times 0.15 mm, length of parallel part: 12 mm, total length: 38 mm). Reported mechanical data are averages of 3-5 independent experiments and all errors are standard deviations. The tensile moduli were calculated from the slopes of the linear region in the strain regime of 0-0.5%. The area under the stress-strain curves was determined to quantify the toughness. A Hönle Bluepoint 4 Ecocure UV lamp equipped with an optical fiber and a 320-390 nm filter and an intensity of 900-950 mW/cm² was used as a light source for the UV-light bonding/debonding experiments. Surface temperatures of thin films were monitored with an Optrix PI Connect infrared camera (model PI 160) from Roth AG (Switzerland).

Preparation of UPy-PEB-UPy Films with UV Absorber. Targeting an absorbance of <1 for a 90 μm thick film, UPy-PEB-UPy (300 mg, 76.7 μmol) was dissolved in anhydrous $CHCl_3$ (4 mL) and a solution of 2-(5-chloro-2H-benzotriazole-2-yl)-6-(1,1-dimethyl-4-methyl-phenol) (0.75 mg, 2.37 μmol ; Tinuvin 326 supplied by Ciba) in $CHCl_3$ was added under stirring. The solution was cast into a poly(tetrafluoroethylene) Petri dish and the solvent was allowed to evaporate under ambient conditions, before solvent residues were removed under reduced pressure to afford a clear, rubbery solid. Films were then produced by compressing-molding the product at 80 °C and 3 tons for 5 min as described above for the neat polymer.

Adhesive Properties and Debonding on Demand. Adhesion properties were investigated using a Zwick/Roell Z010 tensile tester equipped with a 10 kN load cell and mechanical gripping clamps at a strain rate of 10 mm/min at room temperature. Lap joints were made with quartz glass, regular glass, and stainless steel with bond areas of 10 \times 12.5 mm (quartz glass), 10 \times 25.7 mm (regular glass), and 10 \times 10.5 mm (stainless steel). During the bonding process, the joints were mechanically fixed to prevent undesired changes of the bonding area and samples were tested within 1 h after bonding. Reported shear strength test results are averages of 3-5 samples. Further information is provided in Figure S1 in the Supporting Information.

RESULTS AND DISCUSSION

Supramolecular polymers based on a hydrophobic core of telechelic poly(ethylene-co-butylene) (PEB) that was end-functionalized with either hydrogen-bonding UPy (UPy-PEB-UPy)³⁹ or metal-coordinating 2,6-bis(1'-methylbenzimidazolyl)-pyridine (Mebip) ligands (Mebip-PEB-Mebip)⁴¹ were synthesized as described before (Figure 1). In the latter case, metallosupramolecular polymers of the formula $[Zn_{0.8}Mebip-PEB-Mebip](NTf_2)_{1.6}$ were assembled by coordination to 0.8 equiv. of zinc(II) bistriflimide (Figure 1). The metal:ligand ratio was slightly offset from a stoichiometric balance, based on

the previous finding that the presence of a small amount of free ligands increases the healability of this material upon exposure to UV light, presumably by rendering the metal-ligand binding more dynamic.⁴¹ Dynamic mechanical thermal analysis (DMTA) experiments (see Table S1 and Figure S3 in the Supporting Information) show that the two polymers are glassy below -40 °C, with a tensile storage modulus E' of ~ 2 GPa. Above the glass transition a rubbery plateau is observed in both cases, with an E' of ~ 100 MPa and ~ 10 MPa at 25 °C for $[Zn_{0.8}Mebip-PEB-Mebip](NTf_2)_{1.6}$ and UPy-PEB-UPy, respectively, before the materials fail at ~ 240 and ~ 70 °C. Stress-strain experiments conducted at 25 °C reveal a maximum stress of 5.6 and 3.0 MPa and an elongation at break of 35 and 70% for $[Zn_{0.8}Mebip-PEB-Mebip](NTf_2)_{1.6}$ and UPy-PEB-UPy, respectively (see Table S1 and Figure S4 in the Supporting Information). The mechanical data match previous accounts and are consistent with microphase-segregated morphologies in which the UPy and metal-ligand motifs phase-separate from the rubbery PEB to form hard phases that serve as physical cross-links.^{41,52} It is noted that the room-temperature stiffness and strength and the dissociation temperature of the metallopolymer are considerably higher than those of the hydrogen-bonded material. In the case of UPy-PEB-UPy, we observed a slight increase in stiffness with time, presumably due to ageing, and therefore all experiments were carried out with freshly processed samples.

We have previously shown that on account of nonradiative relaxation pathways, the metal-ligand complexes comprised in this metallopolymer cause rapid heating upon exposure to UV light; under the irradiating conditions applied the surface temperature of a $[Zn_{0.7}Mebip-PEB-Mebip](NTf_2)_{1.4}$ film rose to over 220 °C within 30 s and slightly higher upon longer irradiation.⁴¹ To explore the usefulness of $[Zn_{0.8}Mebip-PEB-Mebip](NTf_2)_{1.6}$ and UPy-PEB-UPy as light-responsive reversible adhesives, we prepared single lap joints with an overlap area of 10 \times 12.5 mm by sandwiching films of the supramolecular polymers of a thickness of 80-100 μm between two substrates (see Figure 2 and Figure S1 in the Supporting Information). Quartz slides, used on account of their transparency in the UV regime where the Zn^{2+} Mebip complexes absorb ($\lambda_{max} = 344$ nm, see Figure S2 in the Supporting Information) were bonded with $[Zn_{0.8}Mebip-PEB-Mebip](NTf_2)_{1.6}$ as the adhesive by exposure to either heat (2 min, 200 °C) or UV light (2 \times 60 s, $\lambda = 320-500$ nm, 900 mW/cm²). Figure 2a shows strikingly that the bonds thus formed were of considerable strength. The adhesive properties were quantitatively explored by shear tests at ambient conditions (Table 1, Figure 3a), which revealed a shear strength of 2.5 ± 0.2 MPa for thermally bonded and 1.8 ± 0.4 MPa for optically bonded samples (Table 1); these values are comparable to those of hot melt adhesives typically used in household applications to bond glass, wood and plastics.⁵³ The shear strength of thermally and optically bonded samples was comparable, even though thermal bonding was carried out at only 200 °C, i.e., below the temperature at which the Zn^{2+} Mebip complexes completely dissociate ($T_{fail} = ca. 240$ °C) (see Figure S4 in the Supporting Information).⁴¹ The shear tests revealed that $[Zn_{0.8}Mebip-PEB-Mebip](NTf_2)_{1.6}$ undergoes adhesive failure, i.e., the polymer delaminates from the quartz substrate (Figure 2d). Attempts to improve the adhesion by bonding at higher temperatures and/or increasing the UV exposure time caused yellowing of the supramolecular adhesive,

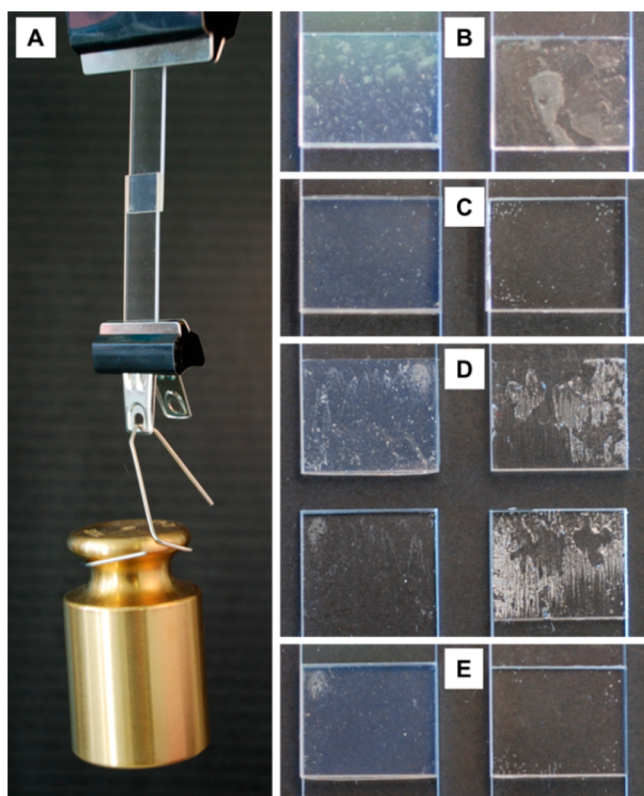


Figure 2. Pictures of lap joints bonded with supramolecular polymers. (a) Quartz glass slides bonded with $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ holding a 500 g weight. b-e) Quartz glass slides bonded with $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ (left) and UPy-PEB-UPy (right). (b) Unbonded overlap. (c) Thermally bonded $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$; 200 °C, 2 min; UPy-PEB-UPy: 80 °C, 5 min). (d) Bonded as in c and separated after shear test (adhesive failure in the case of $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ and cohesive failure for UPy-PEB-UPy). (e) Separated as in d and rebonded as in c.

Table 1. Shear Test Results of Quartz Lap Joints Bonded with $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ or UPy-PEB-UPy

	shear stress (MPa)	
	$[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$	UPy-PEB-UPy
thermally bonded ^a	2.5 ± 0.2	0.9 ± 0.1
thermally rebonded ^{a,d}	2.5 ± 0.1	1.0 ± 0.1
UV bonded ^b	1.8 ± 0.4	1.2 ± 0.1 ^c
UV rebonded ^{b,d}	2.3 ± 0.1	1.6 ± 0.2 ^c

^aThermal bonding was achieved by exposure to heat (2 min, 200 °C for $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$; 5 min, 80 °C for UPy-PEB-UPy). ^bUV bonding was achieved by exposure to UV light (2 × 60 s, $\lambda = 320\text{--}500$ nm, 900 mW/cm²). ^c0.25% w/w of Tinuvin 326 was added as a light-heat converter to the polymer. ^dSamples were subjected to a shear-test experiment until the bonds failed, and the lap joints were rebonded using the original bonding conditions, but without applying additional adhesive. All measurements were repeated 5 times ($n = 5$) and the errors are standard deviations.

indicative of degradation, which was also observed by TGA measurements (see Figure S5 in the Supporting Information).

Quartz slides were also thermally bonded (5 min, 80 °C) with UPy-PEB-UPy, to create lap joints with a shear strength of 0.9 MPa (Table 1, Figure 3b), i.e., about half of that of lap joints bonded with $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ (vide supra). For comparison, samples were also thermally bonded to

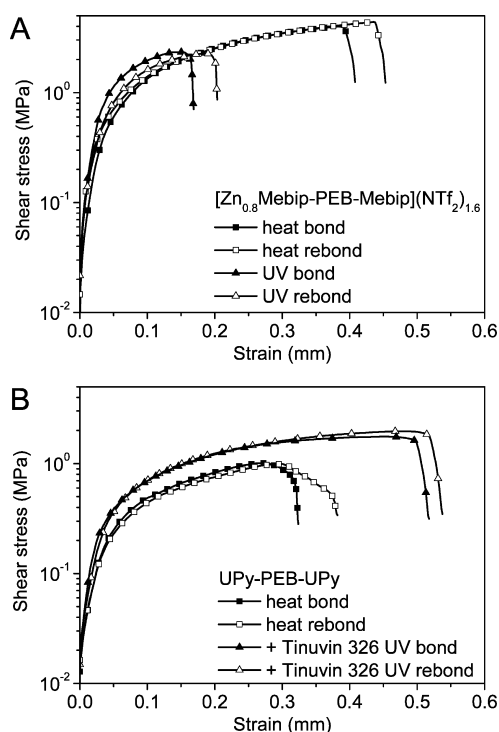


Figure 3. Shear tests of quartz lap joints bonded with (a) $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ or (b) UPy-PEB-UPy. Bonding was achieved by either exposure to heat (2 min, 200 °C for $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$; 5 min, 80 °C for UPy-PEB-UPy) (■) or UV light (2 × 60 s, $\lambda = 320\text{--}500$ nm, 900 mW/cm²) (▲). For rebonding experiments (□, △), samples were first bonded thermally or by UV light, subjected to a shear-test experiment until the bond failed, and the lap joint was rebonded using their respective original bonding conditions, but without applying additional adhesive, as described in Figure S1 in the Supporting Information. The graphs show representative curves selected from series of 5 measurements per condition.

a stainless steel substrate, and shear tests reveal comparable shear strengths (1.0 MPa ± 0.2 MPa) (see Table S2 in the Supporting Information). Unlike the metallosupramolecular polymer, UPy-PEB-UPy does not absorb light at wavelengths above 320 nm (see Figure S2 in the Supporting Information) and can therefore not be (de)bonded in its neat form with the light source used here. Therefore, 0.25% w/w of a UV absorber (Tinuvin 326) (Figure 1) with absorption maxima at 311 and 348 nm (see Figure S2 in the Supporting Information) was added to UPy-PEB-UPy in order to render the hydrogen-bonding supramolecular polymer UV light-sensitive, and convert the absorbed energy into heat by way of radiationless decay.⁵⁴ When lap joints bonded with UPy-PEB-UPy/Tinuvin 326 were irradiated with UV light ($\lambda = 320\text{--}390$ nm, 950 mW/cm²), the sample reached a maximum temperature of 78 °C within 40 s (see Figure S6 in the Supporting Information). The fact that a much higher maximum temperature (167 °C) was reached within seconds when free-standing films were irradiated (see Figure S6 in the Supporting Information), indicates that the quartz slides act as heat sinks and that thermal transport is an important feature to be considered. Lap joints with UPy-PEB-UPy/Tinuvin 326 blends were then bonded by exposure to UV light (2 × 60 s, $\lambda = 320\text{--}500$ nm, 900 mW/cm²), and a shear strength of 1.2 MPa was measured (Table 1, Figure 3b). A comparison with thermally formed bonds using either the neat UPy-PEB-UPy or its blend with Tinuvin 326

(see Table S2 in the Supporting Information) shows that neither the presence of the UV absorber nor the bonding method has a significant influence on the bond strength. In contrast to the metallopolymer, UPy-PEB-UPy shows a cohesive failure mode (Figure 2d), which we explain with the well-defined and low dissociation temperature of this material, which translates into a lower viscosity during the bonding process and better adhesion.

To probe stimulus-induced (de)bonding on demand scenarios, a series of debonding experiments was conducted. Thus, thermally or optically bonded quartz glass lap joints with either $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ or UPy-PEB-UPy/Tinuvin 326 were mounted in a tensile tester and placed under a constant force (ca. 50 and 30 N for $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ and UPy-PEB-UPy, respectively) (Figure 4).

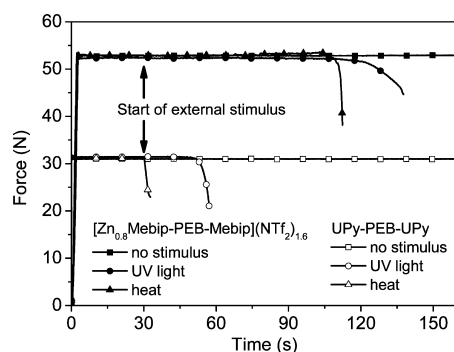


Figure 4. Debonding experiment with quartz glass lap joints thermally bonded with $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ (200 °C, 2 min) and UPy-PEB-UPy/Tinuvin 326 (80 °C, 5 min). The lap joints were placed in a tensile tester, a force of 53 N for $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ (■, ●, ▲), or 31 N for UPy-PEB-UPy (□, ○, △) was applied, and the force was monitored as a function of time. Either no stimulus was applied (■, □) or the sample was exposed to UV light (320–500 nm, 900 mW/cm²) (●, ○) or heat (airflow of ca. 300 °C) (▲, △). The graph shows representative curves selected from series of 3 measurements per condition.

Under these conditions neither creep nor failure were observed on a time-scale of 5 min (data not shown) for any of the samples. A 500 g weight was suspended from a bonded lap joint and failure was not observed within a period of 3 months. While under load, the lap joints were either irradiated with UV light ($\lambda = 320\text{--}500$ nm, 900 mW/cm²) or hot air (temperature ca. 300 °C), the force was measured as a function of time, and the time to failure recorded (see Table S3 in the Supporting Information). Under the specific conditions applied, bonds formed with $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ failed after 80 s of irradiation with UV light and 75 s upon heating. Samples bonded with UPy-PEB-UPy failed after 2 s and 30 s when exposed to heat and UV light, respectively. The faster debonding observed for UPy-PEB-UPy is consistent with its lower dissociation temperature in comparison to $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ (70 vs. > 200 °C) (see Figure S3 in the Supporting Information).^{41,52} In contrast to $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$, where optical and thermal debonding are equally fast, the UPy-PEB-UPy/Tinuvin 326 system exhibit much slower optical than thermal debonding. This is due to the low light-heat converter content used, which translates into much lower absorbance of incident light (see Figure S2 in the Supporting Information). Thus, it can be expected that an

increase in the sensitizer content would increase the rate of optical debonding in this system.

The reversible nature of the (dis)assembly of $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ and UPy-PEB-UPy was further utilized to rebond shear-tested failed samples (Figure 2d,e) using the original optical and thermal bonding conditions as described above. Gratifyingly, the shear strength of the rebonded lap joints was essentially identical to the original value for each system (Table 1). Thus, these results demonstrate that $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ and UPy-PEB-UPy supramolecular polymers can be bonded, debonded and rebonded on demand repeatedly with essentially no changes in their mechanical properties.

CONCLUSIONS

One of the attractive features of supramolecular polymers is the dynamic nature of the supramolecular motifs. The equilibrium of the polymerization/depolymerization of supramolecular materials can be adjusted by the addition of well-defined sets of stimuli (e.g., heat, light). Here, we have demonstrated the stimuli-responsive behavior of metal-coordinate and hydrogen-bonding motifs and have explored the adhesive properties of $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ and UPy-PEB-UPy supramolecular polymers. The materials were used to bond quartz slides using either thermal or light bonding conditions. Tensile tests revealed appreciable shear strengths for both supramolecular polymers. When $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ and UPy-PEB-UPy lap joints were placed under constant force and exposed to either heat or UV light, the materials debonded within seconds. Moreover, debonded samples of both $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ and UPy-PEB-UPy were rebonded when exposed to original bonding conditions. This work demonstrates that supramolecular polymers can be bonded, debonded, and rebonded on demand. Recent studies from our group have shown that the mechanical properties of the supramolecular polymers used here can be tailored by introduction of cellulose nanocrystals,^{43,45} and one can expect that this approach can also be used to increase the maximum shear stress when used as adhesives.

ASSOCIATED CONTENT

Supporting Information

Characterization by NMR, IR, and GPC; tables with debonding, shear test, and mechanical data; absorption spectra of solutions and films; a schematic of the bonding and debonding experiments; graphs documenting shearing test experiments of UV- and heat-bonded lap joints with $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ and UPy-PEB-UPy; DMTA and tensile test data for $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ and UPy-PEB-UPy; TGA experiments; and a surface temperature profile for UPy-PEB-UPy + Tinuvin 326 upon UV irradiation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Oehlenschlaeger, K. K.; Guimard, N. K.; Brandt, J.; Mueller, J. O.; Lin, C. Y.; Hilf, S.; Lederer, A.; Coote, M. L.; Schmidt, F. G.; Barner-Kowollik, C. Fast and Catalyst-Free Hetero-Diels-Alder Chemistry for on Demand Cyclable Bonding/Debonding Materials. *Polym. Chem.* **2013**, *4*, 4348–4355.
- (2) Aubert, J. H. Note: Thermally Removable Epoxy Adhesives Incorporating Thermally Reversible Diels-Alder Adducts. *J. Adhes.* **2003**, *79*, 609–616.
- (3) Becher, P.; Flegel, H.; Herrmann, M.; Kurzmann, P.; Bauer, J.; Bauer, M.; Krüger, H.; Neumann-Rodekrich, J.; Schneider, J.; Hirthammer, M. Adhesive System to Form Reversible Glued Joints. WO 00/05288, February 3, 2000.
- (4) Keitle-Telgenbüscher, K.; Engeldinger, H. K.; Grünauer, J. Inductively Heatable Adhesive Tape with Differential Solubility Characteristics. WO2011085873 A1, 2010.
- (5) Luo, X.; Lauber, K. E.; Mather, P. T. A Thermally Responsive, Rigid, and Reversible Adhesive. *Polymer* **2010**, *51*, 1169–1175.
- (6) Northen, M. T.; Greiner, C.; Arzt, E.; Turner, K. L. A Gecko-Inspired Reversible Adhesive. *Adv. Mater.* **2008**, *20*, 3905–3909.
- (7) Dittmers, H.-J.; Stock, J.; Thorns, D. Pressure-Sensitive Adhesive, Process for Producing the Same and Its Use. WO9412582A1, 1994.
- (8) Inglis, A. J.; Nebhani, L.; Altintas, O.; Schmidt, F. G.; Barner-Kowollik, C. Rapid Bonding/Debonding on Demand: Reversibly Cross-Linked Functional Polymers Via Diels-Alder Chemistry. *Macromolecules* **2010**, *43*, 5515–5520.
- (9) Allies, V. R.; Zimmermann, W. D. Debondable Cyanoacrylate Adhesive Composition. GB1529105, 1976.
- (10) Kirsten, C.; Ferencz, A.; Hirthammer, M. Adhesives Containing Activatable Debonding Agents and Process for Bonding and Debonding. DE19904835A1, 2000.
- (11) Kreckel, K. W.; Karim, N. Removable Adhesive Tape. WO9211332A1, 1992.
- (12) Nijhuis, W. A. Multi-Layer Laminate Structure with Reversible Bonding. EP2517856A1, 2012.
- (13) Zhang, C.; Orosco, M. M.; Yu, X.; Krkibir, F. N.; Thompson, M. E. Reversible Adhesives. WO 2012/048128 A2, 2012.
- (14) Kasprzak, K. A. Method for Removing Tacky Adhesives and Articles Adhered Therewith. 4,324,595, April 13, 1982.
- (15) Grof, T. Tape Releasing Composition and Method of Using Same. 4 867 981, September 19, 1989.
- (16) Adler, M. Method and Composition for Removing Adhesive Bandages. U.S. 6 436 227 B1, August 20, 2002.
- (17) Webster, I. Adhesives. US 6 184 264 B1, February 6, 2001.
- (18) Kawate, K.; Kanki, T. Heat Debondable Adhesive Composition and Adhesion Structure. WO0040648, 2000.
- (19) Paul, C. W.; Carter, J. T.; Morrison, B. D. Hot Melt Adhesive for Packaging Applications. EP1847579A1, 2007.
- (20) Rule, J. D.; Lewandowski, K. M.; Determan, M. D. Debondable Adhesive Article, Fabrication and Use on Adherends. U.S. 20100316845A1, 2010.
- (21) Sjong, A. Thermoplastic Coating and Removal Using Bonding Interface with Catalytic Nanoparticles. WO2011059625A1, 2011.
- (22) Nguyen, M. K.; Huynh, C. T.; Lee, D. S. Ph-Sensitive and Bioadhesive Poly(B-Amino Ester)-Poly(Ethylene Glycol)-Poly(B-Amino Ester) Triblock Copolymer Hydrogels with Potential for Drug Delivery in Oral Mucosal Surfaces. *Polymer* **2009**, *50*, 5205–5210.
- (23) Sudre, G.; Olanier, L.; Tran, Y.; Hourdet, D.; Creton, C. Reversible Adhesion between a Hydrogel and a Polymer Brush. *Soft Matter* **2012**, *8*, 8184–8193.
- (24) Saito, K.; Sakai, A.; Nate, K. Light-Sensitive Peelable Adhesive Tapes and Sheets and Their Manufacture. JP2002212521A, 2002.
- (25) Liou, K.; Khemani, K. C.; Wudl, F. Novel Adhesives Based on Poly(Isocyanates). *Macromolecules* **1991**, *24*, 2217–2220.
- (26) Cordier, P.; Tournilhac, F.; Soulie-Ziakovic, C.; Leibler, L. Self-Healing and Thermoreversible Rubber from Supramolecular Assembly. *Nature* **2008**, *451*, 977–980.
- (27) Bosman, A. W.; Sijbesma, R. P.; Meijer, E. W. Supramolecular Polymers at Work. *Mater. Today* **2004**, *7*, 34–39.
- (28) Chen, Y.; Kushner, A. M.; Williams, G. A.; Guan, Z. Multiphase Design of Autonomic Self-Healing Thermoplastic Elastomers. *Nat. Chem.* **2012**, *4*, 467–472.
- (29) van Gemert, G. M. L.; Peeters, J. W.; Söntjens, S. H. M.; Janssen, H. M.; Bosman, A. W. Self-Healing Supramolecular Polymers in Action. *Macromol. Chem. Phys.* **2012**, *213*, 234–242.
- (30) Li, S.-L.; Xiao, T.; Lin, C.; Wang, L. Advanced Supramolecular Polymers Constructed by Orthogonal Self-Assembly. *Chem. Soc. Rev.* **2012**, *41*, 5950–5968.
- (31) Harris, R. D.; Auletta, J. T.; Motlagh, S. A. M.; Lawless, M. J.; Perri, N. M.; Saxena, S.; Weiland, L. M.; Waldeck, D. H.; Clark, W. W.; Meyer, T. Y. Chemical and Electrochemical Manipulation of Mechanical Properties in Stimuli-Responsive Copper-Cross-Linked Hydrogels. *ACS Macro Lett.* **2013**, *2*, 1095–1099.
- (32) Lehn, J.-M. Supramolecular Polymer Chemistry—Scope and Perspectives. *Polym. Int.* **2002**, *51*, 825–839.
- (33) Viswanathan, K.; Ozhalici, H.; Elkins, C. L.; Heisey, C.; Ward, T. C.; Long, T. E. Multiple Hydrogen Bonding for Reversible Polymer Surface Adhesion. *Langmuir* **2005**, *22*, 1099–1105.
- (34) Yamauchi, K.; Lizotte, J. R.; Long, T. E. Thermoreversible Poly(Alkyl Acrylates) Consisting of Self-Complementary Multiple Hydrogen Bonding. *Macromolecules* **2003**, *36*, 1083–1088.
- (35) Calvo-Marzal, P.; Delaney, M. P.; Auletta, J. T.; Pan, T.; Perri, N. M.; Weiland, L. M.; Waldeck, D. H.; Clark, W. W.; Meyer, T. Y. Manipulating Mechanical Properties with Electricity: Electroplastic Elastomer Hydrogels. *ACS Macro Lett.* **2011**, *1*, 204–208.
- (36) Anderson, C. A.; Jones, A. R.; Briggs, E. M.; Novitsky, E. J.; Kuykendall, D. W.; Sottos, N. R.; Zimmerman, S. C. High-Affinity DNA Base Analogs as Supramolecular, Nanoscale Promoters of Macroscopic Adhesion. *J. Am. Chem. Soc.* **2013**, *135*, 7288–7295.
- (37) Jochum, F. D.; Theato, P. Temperature- and Light-Responsive Smart Polymer Materials. *Chem. Soc. Rev.* **2013**, *42*, 7468–7483.
- (38) Ahn, Y.; Jang, Y.; Selvapalam, N.; Yun, G.; Kim, K. Supramolecular Velcro for Reversible Underwater Adhesion. *Angew. Chem. Int. Ed.* **2013**, *52*, 3140–3144.
- (39) Folmer, B. J. B.; Sijbesma, R. P.; Versteegen, R. M.; van der Rijt, J. A. J.; Meijer, E. W. Supramolecular Polymer Materials: Chain Extension of Telechelic Polymers Using a Reactive Hydrogen-Bonding Synthon. *Adv. Mater.* **2000**, *12*, 874–878.
- (40) Lindsay, C. I.; Wouters, S. A. Bulk Manufacturing of Supramolecular Polymer Forming Polymer. US20070149751 A1, June 28, 2007.
- (41) Burnworth, M.; Tang, L.; Kumpfer, J. R.; Duncan, A. J.; Beyer, F. L.; Fiore, G. L.; Rowan, S. J.; Weder, C. Optically Healable Supramolecular Polymers. *Nature* **2011**, *472*, 334–337.
- (42) Fiore, G. L.; Rowan, S. J.; Weder, C. Optically Healable Polymers. *Chem. Soc. Rev.* **2013**, *42*, 7278–7288.
- (43) Coulibaly, S.; Roulin, A.; Balog, S.; Biyani, M. V.; Foster, E. J.; Rowan, S. J.; Fiore, G. L.; Weder, C. Reinforcement of Optically Healable Supramolecular Polymers with Cellulose Nanocrystals. *Macromolecules* **2014**, *47*, 152–160.
- (44) Yuan, J.; Fang, X.; Zhang, L.; Hong, G.; Lin, Y.; Zheng, Q.; Xu, Y.; Ruan, Y.; Weng, W.; Xia, H.; Chen, G. Multi-Responsive Self-Healing Metallo-Supramolecular Gels Based on “Click” Ligand. *J. Mater. Chem.* **2012**, *22*, 11515–11522.
- (45) Biyani, M. V.; Foster, E. J.; Weder, C. Light-Healable Supramolecular Nanocomposites Based on Modified Cellulose Nanocrystals. *ACS Macro Lett.* **2013**, *2*, 236–240.
- (46) Minton, T. K.; Wu, B.; Zhang, J.; Lindholm, N. F.; Abdulagatov, A. I.; O'Patchen, J.; George, S. M.; Groner, M. D. Protecting Polymers

in Space with Atomic Layer Deposition Coatings. *ACS Appl. Mater. Interfaces* **2010**, *2*, 2515–2520.

(47) Perichaud, A. Self-Healing for Space Applications. *Galvano-Organo* **2011**, *79*, 34–36.

(48) Boyne, J. M.; Millian, E. J.; Webster, I. Peeling Performance of a Novel Light Switchable Pressure-Sensitive Adhesive. *Int. J. Adhes. Adhes.* **2001**, *21*, 49–53.

(49) Jacobsson, D. Strong Adhesives for Sensitive Surfaces, High Strength Connections, Soluble at Any Time. *Adhaes.–Kleben Dichten* **2009**, *53*, 29–31.

(50) Tehranchi, A.; Fekrazad, R.; Zafar, M.; Eslami, B.; Kalhori, K. A. M.; Gutknecht, N. Evaluation of the Effects of CO₂ Laser on Debonding of Orthodontics Porcelain Brackets Vs. The Conventional Method. *Lasers Med. Sci.* **2010**, *26*, 563–567.

(51) Dillard, D. A. In *Handbook of Adhesion*, second ed.; Packham, D. E., Ed.; John Wiley & Sons: West Sussex, England, 2005, p 494–496.

(52) Kautz, H.; van Beek, D. J. M.; Sijbesma, R. P.; Meijer, E. W. Cooperative End-to-End and Lateral Hydrogen-Bonding Motifs in Supramolecular Thermoplastic Elastomers. *J. Am. Chem. Soc.* **2006**, *39*, 4265–4267.

(53) Swan, D. G.; Hansen, J. C. Poly(Ester-Amide) Composition. EP 0204315 A2, December 10, 1986.

(54) Zweifel, H.; Amos, S. E. *Plastics Additives Handbook*, 5th ed.; Carl Hanser: Munich, 2001; p 1148.