ACS APPLIED MATERIALS & INTERFACES

Research Article

www.acsami.org

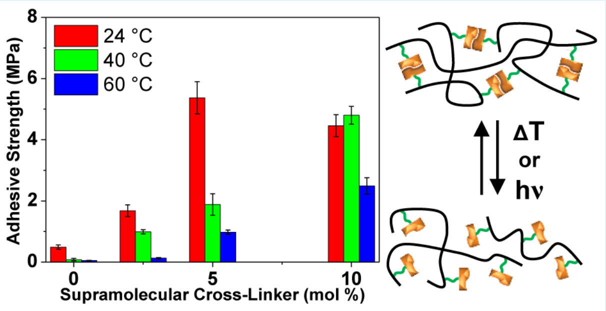
Supramolecular Cross-Links in Poly(alkyl methacrylate) Copolymers and Their Impact on the Mechanical and Reversible Adhesive Properties

Christian Heinzmann,[†] Ulrich Salz,[‡] Norbert Moszner,[‡] Gina L. Fiore,[†] and Christoph Weder*,[†]

[†]Adolphe Merkle Institute, University of Fribourg, Chemin des Verdiers 4, CH-1700 Fribourg, Switzerland

[‡]Ivoclar Vivadent AG, Bendererstrasse 2, FL-9494 Schaan, Liechtenstein

S *Supporting Information*



ABSTRACT: Hydrogen-bonded, side-chain-functionalized supramolecular poly(alkyl methacrylate)s were investigated as light- and temperature-responsive reversible adhesives that are useful for bonding and debonding on demand applications. Here, 2-hydroxyethyl methacrylate (HEMA) was functionalized with 2-ureido-4[1*H*]pyrimidinone (UPy) via a hexamethylenediisocyanate (HMDI) linker, to create a monomer (UPy-HMDI-HEMA) that serves to form supramolecular cross-links by way of forming quadruple hydrogen bonded dimers. UPy-HMDI-HEMA was copolymerized with either hexyl methacrylate or butyl methacrylate to create copolymers comprising 2.5, 5, or 10 mol % of the cross-linker. The mechanical properties of all (co)polymers were investigated with stress−strain experiments and dynamic mechanical analysis. Furthermore, the adhesive properties were studied at temperatures between 20 and 60 °C by testing single lap joints formed with stainless steel substrates. It was found that increasing the concentration of the UPy-HMDI-HEMA cross-linker leads to improved mechanical and adhesive properties at elevated temperatures. Concurrently, the reversibility of the bond formation remained unaffected, where rebonded samples displayed the same adhesive strength as regularly bonded samples. Debonding on demand abilities were also tested exemplarily for one copolymer, which for light-induced debonding experiments was blended with a UV-absorber that served as light−heat converter. Single lap joints were subjected to a constant force and heated or irradiated with UV light until debonding occurred. The necessary debonding temperature was comparable for direct heating and UV irradiation and varied between 28 and 82 °C, depending on the applied force. The latter also influenced the debonding time, which under the chosen conditions ranged from 30 s to 12 min.

KEYWORDS: *supramolecular polymer, hydrogen-bonding, stimuli-responsive, reversible adhesive, debond on demand, (UV) light*

■ INTRODUCTION

Supramolecular polymeric materials enjoy growing interest in the scientific community, due to the unusual property matrix that is accessible through the principle of self-assembly.[1−4] The formation of supramolecular bonds is generally reversible, and the equilibrium between the disassembled and assembled state can usually be shifted by an external stimulus, which causes a change of some of the materials properties.[4−6] Depending on the supramolecular motif, this is possible by exposure to chemicals[6] or solvents,[7] change of pH[8] or temperature,[9] irradiation with light,[9,10] application of electricity,[11,12] and redox environments,[13] among others. The quadruple hydrogen-bonded 2-ureido-4[1*H*]pyrimidinone (UPy) motif, which features a high dimerization constant and is easy to synthesize and functionalize,[7,14] has become a widely utilized building block in many supramolecular polymers,[1,7,14−22] both as a linear chain extender[23−25] and as a cross-linker.[19,21,22,25] Initial work on UPy-containing supramolecular polymers focused on studies in solution, before the advantages of reversible bond formation in the context of melt-processing were explored.[26,27] Later, it was shown that the reversibility and stimuli-responsiveness of UPy dimers can serve to enable many interesting features, such as self-healing,[10,28,29] shape-memory,[25,30−32] mechanochemistry,[33,34] or (de)bonding on demand when used as an adhesive.[35,36] In general, the field of UPy-functionalized supramolecular assemblies is vast, with hundreds of references to be found. Most of the described work deals with relatively small polymeric or oligomeric structures with UPy being incorporated in the main chain,[23,37,38] forming discotic arrangements or nanofibers for improved mechanical properties comparable to thermoplastic elastomers.[1,39] The same trend can be found in a large variety of polymers side-chain functionalized with UPy, including poly(acrylate),[40] poly(methacrylate),[41] poly(acrylamide),[21] poly(norbornene),[42]

Received: March 4, 2015
Accepted: June 5, 2015
Published: June 5, 2015

DOI: 10.1021/acsami.5b01939
ACS Appl. Mater. Interfaces 2015, 7, 13395−13404

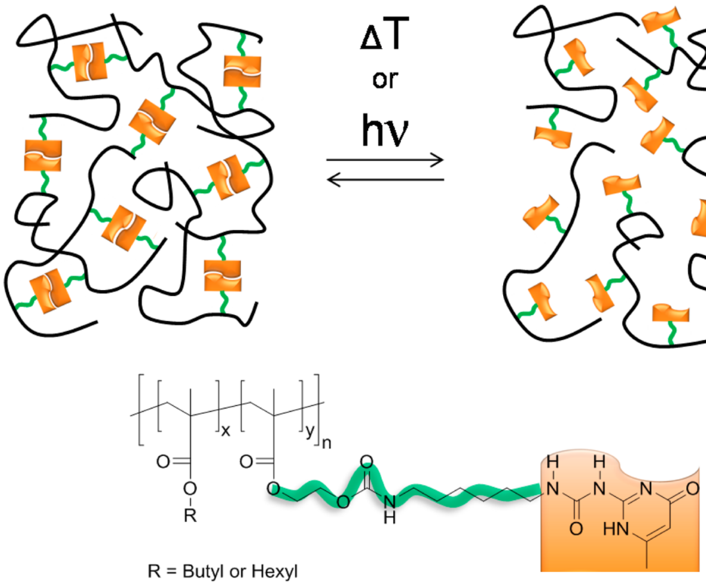
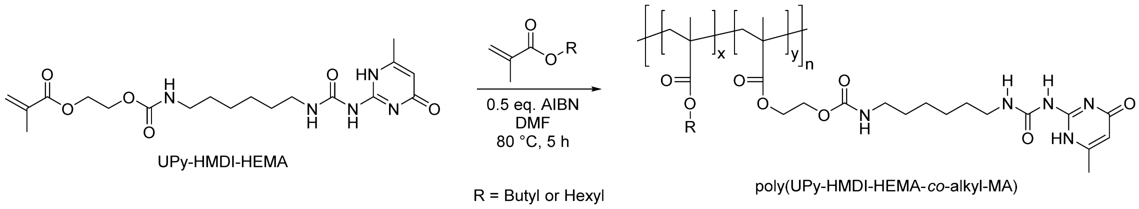


Figure 1. Schematic representation of the heat or (UV)-light triggered disassembly of methacrylic copolymers functionalized with UPy side-chains from a cross-linked to a linear state (top). Chemical structure of the (co)polymers investigated in this study (bottom).

Scheme 1. Synthesis of Poly(UPy-HMDI-HEMA-*co*-hexyl-MA) and Poly(UPy-HMDI-HEMA-*co*-butyl-MA) by Free-Radical Copolymerization of UPy-HMDI-HEMA with Hexyl Methacrylate or Butyl Methacrylate



and poly(styrene).[43] Rheology measurements revealed that strong hydrogen bonding side-chains such as UPy imitate chain entanglements,[21] but with a lower required molecular weight between such physical cross-links.[44] The broad applicability and versatility of UPy to functionalize existing polymers makes it feasible to add new features. Indeed, the reversible bond formation makes supramolecular polymers perfect candidates for many different applications, such as processable, reversible adhesives,[40,45] which can offer the formation of strong bonds between two parts and also satisfy the demand of easy separation when needed. Recently, different concepts of reversible adhesives based on supramolecular polymers have been explored.[31,40,46−48] We previously functionalized a telechelic poly(ethylene-*co*-butylene) (PEB) with either self-complementary hydrogen-bonding UPy motifs or 2,6-bis(1′-methylbenzimidazolyl)pyridine ligands, which can coordinate to metal ions and form a linear metallosupramolecular polymer.[35] In the latter case, light−heat conversion is facilitated by the ultraviolet light-absorbing metal−ligand motifs, whereas in the case of the former, a UV-absorber was added for this purpose. Single lap joints in which the supramolecular polymers were sandwiched between two glass, quartz, or stainless steel substrates, and which were bonded by exposure to either UV light or heat, displayed a shear strength of 0.9−1.2 (hydrogen-bonded) and 1.8−2.5 MPa (metallosupramolecular), respectively. Although debonding and subsequent rebonding were readily possible by exposure to light or heat, the telechelic architecture of the supramolecular building blocks and the low glass transition temperature (T_g) of the poly(ethylene-*co*-butylene) core employed, caused our materials to exhibit low strength and stiffness, which translated into a limited adhesive strength. To improve this important characteristic, we embarked on the investigation of two series of poly(alkyl methacrylate)s in which the UPy motif functions as a reversible supramolecular cross-linker (Figure 1).

In such copolymers, property modification is straightforward through the choice and concentration of appropriate comonomers. The integration of a UPy functionality with a polymerizable methacrylic monomer (2-isocyanatoethyl methacrylate, IEMA) was already reported by Long and coworkers in 2003,[22] who studied the influence of UPy-based supramolecular cross-links on the mechanical properties of such copolymers. UPy-IEMA has subsequently been used by other research groups,[21,32] and several design modifications have been explored, such as the introduction of a spacer between the UPy and the (meth)acrylic monomer, e.g., as reported by Meijer and coworkers,[49] UPy-HMDI-HEMA, formed by the coupling UPy and 2-hydroxyethyl methacrylate (HEMA) with hexamethylene diisocyanate (HMDI) (Scheme 1).

Although several research groups have explored the adhesive properties of hydrogen-bonded supramolecular polymers,[22,40,50] a systematic investigation in which the suitability of UPy-functionalized poly(alkyl methacrylate)s for (de)-bonding on demand applications was related to their composition has, to our best knowledge, not been carried out. We note that in the context of reversible adhesive characteristics, the influence of temperature on the adhesive strength is a key aspect and that both high- as well as low-T_g

adhesives are practically useful. Because methacrylic copolymers permit (as will be shown) to access and probe both these regimes, we copolymerized UPy-HMDI-HEMA with either hexyl methacrylate or butyl methacrylate to produce both glassy and rubbery (co)polymers comprising 2.5, 5, or 10 mol % of the cross-linker (Scheme 1). The mechanical properties of these materials were investigated and correlated with the (reversible) adhesive properties in a temperature regime between 24 and 60 °C.

■ EXPERIMENTAL SECTION

Materials. All chemicals were purchased from Sigma-Aldrich. Butyl methacrylate and hexyl methacrylate were passed over basic alumina prior to use. Chloroform and dimethylformamide (DMF) were dried over molecular sieves (3 and 4 Å, respectively). Triethylamine was dried over 4 Å molecular sieves. All other chemicals were used as received. UPy-hexamethylene diisocyanate-2-hydroxyethyl methacrylate (UPy-HMDI-HEMA) was synthesized as reported earlier,[49] with modifications that are described in the Supporting Information.

Methods. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker Avance III spectrometer in $CDCl_3$ unless indicated otherwise. Chemical shifts are referenced against the signal of residual $CHCl_3$ at 7.26 ppm. Molecular weights were determined by size exclusion chromatography (SEC) ($CHCl_3$, 40 °C, 1.0 mL/min, concentration ~ 1 mg/mL) using multiangle laser light scattering (MALLS) (λ = 658 nm, 25 °C) and refractive index detection (λ = 658 nm, 40 °C). A Varian 5 μm mixed-C guard column and two SEC 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 SEC. The incremental refractive index (d*n*/d*c*) was estimated by a single-injection method with an assumption of 100% mass recovery from the columns. Thermogravimetric analyses (TGA) were conducted under N_2 atmosphere using a Mettler-Toledo Star^e system thermogravimetric analyzer in the range of 35 to 600 °C with a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) measurements were performed under N_2 atmosphere using a Mettler-Toledo Star^e system (heating/cooling rate 10 °C/min, range −70 to +200 °C unless indicated otherwise). Glass transition temperatures, T_g, are reported from the second heating cycle and melting temperatures, T_m, for the monomer are reported from the first heating cycle. FT-IR spectra were recorded with a PerkinElmer Spectrum 65 spectrometer with a resolution of 2 cm^{-1} and 4 scans per sample.

Synthesis of Copolymers. A representative example of the copolymerization of 2.5 mol % UPy-HMDI-HEMA with 97.5 mol % hexyl methacrylate is given. All other copolymers, as well as the reference homopolymers poly(hexyl methacrylate) and poly(butyl methacrylate), were synthesized in an identical manner. Hexyl methacrylate (4.63 mL, 23.5 mmol, 97.5 equiv) and UPy-HMDI-HEMA (255 mg, 602 μmol, 2.5 equiv) were dissolved in anhydrous DMF (20 mL) under N_2 atmosphere. Azobis(isobutyronitrile) (AIBN) was added (19.8 mg, 120 μmol, 0.5 equiv), the round-bottomed reaction flask was placed in an oil bath that had been preheated to 80 °C, and the mixture was stirred at this temperature for 5 h under nitrogen. The reaction mixture was subsequently cooled to room temperature and the polymer was precipitated into cold methanol. The crude polymer was dissolved in $CHCl_3$ (20 mL) and precipitated again into cold methanol (500 mL). The product was filtered off, washed with an additional portion of methanol (50 mL) and dried under high vacuum for 2 d. 2.99 g of a clear, sticky solid were isolated.

Preparation of Polymer Films. Polymer films were produced by compression molding with a Carver CE Press at elevated temperatures (140 °C, 1−3 tons of pressure, 3−5 min in the case of the butyl methacrylate (co)polymers; 80−120 °C, 1 ton of pressure, 3 min in the case of the hexyl methacrylate (co)polymers). The film thickness was controlled by using spacers; films of a thickness of 200−400 μm were used for DMA and stress−strain experiments, whereas the thickness was reduced to 90−100 μm for adhesive experiments. Films of 10 mol % UPy poly(UPy-HMDI-HEMA-*co*-hexyl-MA) comprising additionally 0.25 wt % of the ultraviolet light absorber 2-(5-chloro-2H-benzotriazole-2-yl)-6-(1,1-dimethylehtyl)-4-methyl-phenol (Tinuvin 326 supplied by the former Ciba Specialty Chemicals Company) were prepared as previously reported.[35]

Mechanical Testing. Dynamic mechanical analyses (DMA) were conducted under N_2 atmosphere on a TA Instruments DMA Q800 with a heating rate of 5 °C/min, a frequency of 1 Hz, and an amplitude of 15 μm in the range of −40 to +160 °C with an equilibration time of 3 min at the lowest temperature, unless indicated otherwise. Stress−strain experiments were conducted with dumbbell-shaped samples (width at the narrowest part = 2.1 mm) at 24 ± 1 °C with a TA Instruments DMA Q800 with a strain rate of 5%/min, except for 0 and 2.5 mol % poly(UPy-HMDI-HEMA-*co*-butyl-MA), which on account of their high elongation at break were tested with a Zwick/Roell Z010 tensile tester equipped with a 200 N load cell and mechanical grippers with a strain rate of 300%/min. The tensile (Young's) modulus was calculated from the slope of the linear region of the stress−strain curves. Reported mechanical data are averages of 3−5 independent experiments and all errors are standard deviations.

Adhesive Properties. The adhesion properties of the (co)polymers were investigated using a Zwick/Roell Z010 tensile tester equipped with a 10 kN load cell, a controlled temperature chamber, and mechanical gripping clamps at a strain rate of 1 mm/min at 24 ± 1, 40 ± 2, or 60 ± 2 °C. At elevated temperatures (40 and 60 °C), the tests were started 1 min after the temperature had equilibrated at the target value. Single lap joints were made with stainless steel or with quartz glass with bond areas of 10 mm × 10 mm or 10 mm × 12 mm, respectively, and the substrate surface was cleaned with isopropyl alcohol before applying the polymer. During the bonding process with heat (5 min in a preheated oven at elevated temperatures; 140 °C for butyl methacrylate (co)polymers, 80−120 °C for hexyl methacrylate (co)polymers) or with UV light (λ = 320−500 nm, 2500 mW/cm^2, 2 × 40 s for the 10 mol % UPy poly(UPy-HMDI-HEMA-*co*-hexyl-MA comprising 0.25 wt % UV sensitizer), the joints were mechanically fixed to prevent undesired changes of the bonding area and samples were tested within 1 h after bonding. After a sample failed in an adhesive experiment, the lap joint was rebonded using the same protocol. Reported shear strength values are averages of 3−5 samples and are quoted ± standard deviation. Debonding experiments were carried out with either heat (heating rate: 5 °C/min) or UV/visible light (λ = 320−500 nm, 2500 mW/cm^2) as a stimulus, where the samples were subjected to constant loads until debonding occurred. In the case of UV light, the surface temperature of the lap joint was measured with an Optris PI Connect infrared camera (model PI 160).

■ RESULTS AND DISCUSSION

The UPy-functionalized monomer UPy-HMDI-HEMA was synthesized by functionalizing 2-hydroxyethyl methacrylate (HEMA) with 2-ureido-4[1*H*]pyrimidinone (UPy) via a hexamethylenediisocyanate linker, as previously reported[49] with minor modifications that are described in the Supporting Information. UPy-HMDI-HEMA was separately copolymerized with hexyl methacrylate (hexyl-MA) and butyl methacrylate (butyl-MA) to afford copolymers poly(UPy-HMDI-HEMA-*co*-hexyl-MA) and poly(UPy-HMDI-HEMA-*co*-butyl-MA) comprising 2.5, 5, or 10 mol % of the cross-linker (Scheme 1). The comonomers were selected with the objective to create copolymers that are either in their rubbery (hexyl-MA) or glassy (butyl-MA) state at ambient temperature. The (co)polymerization reactions were carried out in DMF solutions at a monomer concentration of 20 wt %, a temperature of 80 °C, and using 0.5 mol % AIBN as initiator (Scheme 1, Table 1). The reactions were quenched after 5 h to limit the monomer conversion to *ca.* 70%. The molecular weights and dispersity

Table 1. General Properties of the (Co)Polymers Studied

UPy content (mol %)			
feed	found[a]	M_n[b]	$Đ$[b]
poly(UPy-HMDI-HEMA-*co*-hexyl-MA)			
0	0	193 600	1.84
2.5	2.4	50 700	1.44
5	4.3	109 900	2.06
10	8.9	61 600	1.51
poly(UPy-HMDI-HEMA-*co*-butyl-MA)			
0	0	29 000	2.04
2.5	2.7	83 600	2.76
5	4.3	42 700	1.52
10	9.6	98 500	1.57

[a] Determined by ^{1}H NMR spectroscopy. [b] Determined by size exclusion chromatography.

index ($Đ$) of the polymers were determined by size exclusion chromatography (SEC) in chloroform.

Table 1 shows that the number-average molecular weight (M_n) and $Đ$ range from *ca.* 29 000 to 194 000 and from *ca.* 1.5 to 2.8, respectively, with no clear correlation to the monomer feed. The actual UPy concentration in the copolymers was investigated by ^{1}H NMR spectroscopy (Supporting Information Figures S2−S9) and was found to be in good agreement with the monomer feed. This finding mirrors the results previously reported by Long and coworkers[22] for the copolymerization of UPy-IEMA and butyl acrylate, and UPy-HMDI-HEMA with methyl methacrylate reported by Meijer and coworkers,[49] and confirms that the methacrylic function of UPy-HMDI-HEMA has a similar reactivity as the one in the alkyl (meth)acrylates used. The data suggest that the UPy motif does not promote significant chain transfer, and that the monomer distribution in the copolymer is statistical, as expected for free-radical polymerization of the monomers at hand.[51]

Table 2. Glass Transition Temperatures (T_g) Determined by DSC and DMA Measurements

UPy (mol %)	DSC[a]	DMA[b]
poly(UPy-HMDI-HEMA-*co*-hexyl-MA)		
0	2 ± 1	32 ± 1
2.5	7 ± 1	29 ± 3
5	11 ± 1	33 ± 2
10	25 ± 1	49 ± 1
poly(UPy-HMDI-HEMA-*co*-butyl-MA)		
0	32 ± 1	53 ± 2
2.5	36 ± 2	64 ± 2
5	45 ± 2	76 ± 3
10	59 ± 1	84 ± 1

[a] Temperature quoted corresponds to the minimum of the first derivative of the second heating curve. [b] Temperature quoted corresponds to the maximum of the tan δ curve. Data quoted are averages of 3−5 individual measurements ± standard deviation.

The data compiled in Table 2 and the Supporting Information (Table S1) show that the introduction of UPy-HMDI-HEMA causes a slight increase of T_g; in both (co)polymer series the transition temperature rose by *ca.* 20 °C upon introduction of 10 mol % of the UPy cross-linker, as determined by differential scanning calorimetry (Supporting Information Figure S10) and dynamic mechanical analysis (Figure 2). It is important to note that knowledge of T_g is relevant to interpret the mechanical properties[52−54] and adhesive properties at the various temperatures investigated, and relate them to contributions of the supramolecular cross-links. Evidence for the formation of the latter in the solid state is provided by FT-IR spectra, which show signals at 1697, 1660, 1579, and 1526 cm^{-1}, indicative of UPy hydrogen bonds (Supporting Information Figure S11).[55]

The mechanical properties of the UPy containing poly(alkyl methacrylate)s were first probed as a function of temperature by dynamic mechanical analysis (DMA). Although the hexyl-MA and butyl-MA homopolymers fail just after transitioning through T_g, at 44 and 105 °C, respectively, all copolymers display a rubbery plateau (Figure 2) and a significantly increased failure temperature T_{fail} (T_{fail} is the temperature where the storage modulus drops below 0.1 MPa). Except for the 2.5 mol % UPy containing poly(UPy-HMDI-HEMA-*co*-hexyl-MA), in which T_{fail} increased from 44 (neat poly(hexyl-MA)) to 75 °C, all copolymers fail at *ca.* 130 °C. A comparison with the loss tangent (tan δ) curves, which for both copolymer series reveal a slight increase in T_g and a second transition with a maximum around 130 °C, makes clear that the increased storage modulus is not merely related to the T_g increase. Instead, the data suggest the formation of supramolecular cross-links between chains, which begin to dissociate above *ca.* 100 °C.

The improvement of the mechanical properties of the (co)polymers upon introduction of supramolecular cross-links is further evident if one compares the storage moduli E' at different temperatures (Table 3). In the glassy state (−40 °C), E' of the hexyl-MA (co)polymers increased only slightly from 1200 to *ca.* 1600 MPa upon introduction of 10 mol % UPy-HMDI-HEMA. A similar trend is apparent for the butyl-MA (co)polymers, although the compositions with 5 or 10 mol % UPy-HMDI-HEMA were too brittle to allow DMA measurements at temperatures below 10 °C. At 25 °C and elevated temperatures (40 and 60 °C), the differences between the hexyl-MA and butyl-MA homopolymers and the UPy-containing copolymers are more pronounced and increase with the UPy content. For example, at 40 °C, E' increased from 2 to 144 MPa and from 66 to 1064 MPa upon copolymerizing 10 mol % UPy-HMDI-HEMA with hexyl-MA and butyl-MA, respectively. At 60 °C, the corresponding increases were from not measurable to 9 MPa and from 4 to 586 MPa.

Further investigations of the material's mechanical properties involved stress−strain measurements that were carried out at 24 °C (Figure 3, Table 4). The nonfunctionalized poly(hexyl-MA) displays a stress−strain curve that is characteristic of a non-cross-linked, rubbery polymer with few chain entanglements.[56] The material is characterized by a large strain at break (ε^b) of 570% and a low stress at break (σ^b) of 1.9 MPa. From the low-strain portion of the curve (0.05−0.75%), a Young's modulus (E) of 5.2 MPa was determined. Upon incorporation of UPy-HMDI-HEMA, σ^b increases with the UPy content to reach 5.8 MPa at 10 mol %, whereas ε^b is reduced to 100% and the Young's modulus increases to 82 MPa. The toughness (U_t) remained largely unchanged at a level of around 500 × 10^4 J/m^3. Keeping the DSC and DMA traces in mind (Table 2), which suggest that T_g increases from below to above room temperature as the UPy-HMDI-HEMA content is increased from 0 to 10 mol %, it appears that the changes in mechanical properties are caused by both, the introduction of cross-links and the transition from the rubbery into the glassy state. The

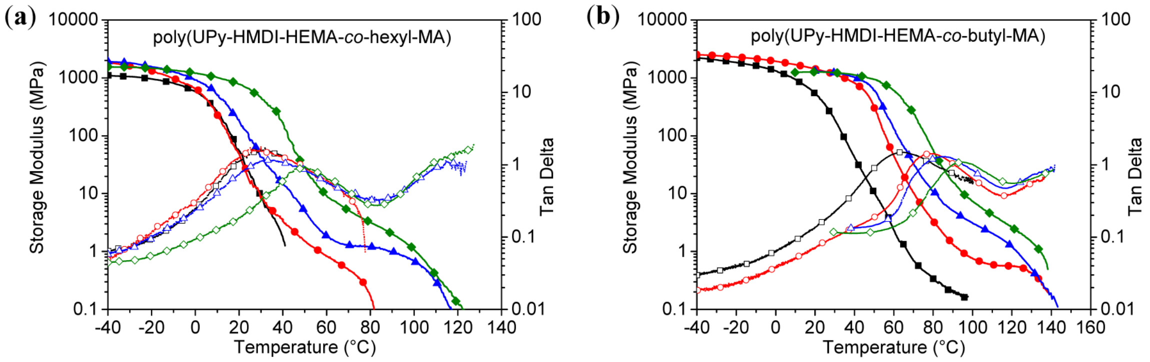


Figure 2. Representative DMA traces of poly(UPy-HMDI-HEMA-*co*-hexyl-MA) (a) and poly(UPy-HMDI-HEMA-*co*-butyl-MA) (b) and the corresponding poly(hexyl-MA) and poly(butyl-MA) homopolymers. The storage modulus E' is represented by solid lines and filled symbols, and the loss tangent (tan δ) is shown by dotted lines and open symbols. The UPy-HMDI-HEMA content in the (co)polymers was 0 mol % (black squares), 2.5 mol % (red circles), 5 mol % (blue triangles), and 10 mol % (green diamonds).

Table 3. Storage Moduli and Failure Temperatures of Poly(UPy-HMDI-HEMA-*co*-hexyl-MA) and Poly(UPy-HMDI-HEMA-*co*-butyl-MA) Determined by DMA

	storage modulus (E') (MPa)				
UPy (mol %)	−40 °C	25 °C	40 °C	60 °C	T_{fail}[a] (°C)
poly(UPy-HMDI-HEMA-*co*-hexyl-MA)					
0	1236 ± 167	25 ± 15	2.0 ± 0.4	n.m.[b]	44 ± 5
2.5	1515 ± 239	25 ± 10	3.2 ± 0.4	0.6 ± 0.3	75 ± 4
5	1618 ± 219	68 ± 12	10 ± 4	1.7 ± 0.2	107 ± 7
10	1564 ± 87	600 ± 17	144 ± 29	9.1 ± 1.0	118 ± 6
poly(UPy-HMDI-HEMA-*co*-butyl-MA)					
0	2077 ± 123	475 ± 76	66 ± 18	3.8 ± 0.8	105 ± 9
2.5	2506 ± 229	1263 ± 173	873 ± 64	37 ± 5	134 ± 6
5	n.m.[b]	1085 ± 167	894 ± 125	241 ± 78	127 ± 9
10	n.m.[b]	1191 ± 92	1064 ± 70	586 ± 16	136 ± 9

[a] T_{fail} is the failure temperature, at which the storage modulus drops below 0.1 MPa. [b] Not measured, as the materials are too brittle (−40 °C) or lack sufficient mechanical strength (60 °C). E' values are averages of 3−5 measurements. Errors are standard deviations.

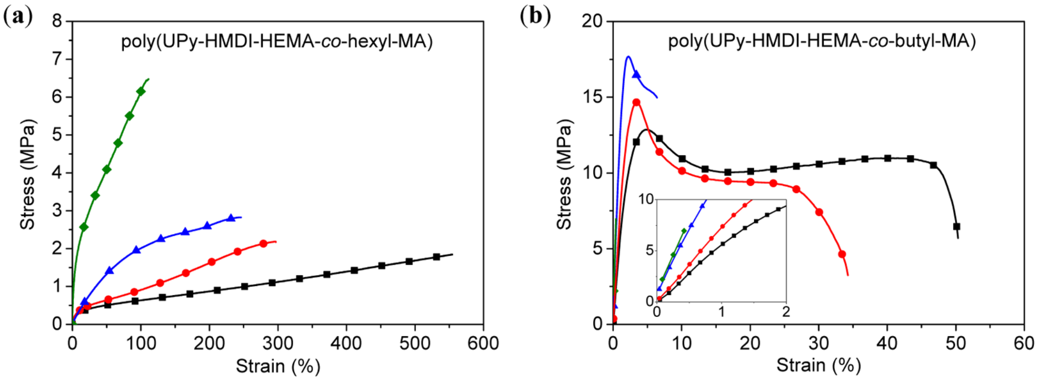


Figure 3. Representative stress−strain curves of poly(UPy-HMDI-HEMA-*co*-hexyl-MA) (a) and poly(UPy-HMDI-HEMA-*co*-butyl-MA) (b) and the corresponding hexyl-MA and butyl-MA homopolymers measured at 24 ± 1 °C. The UPy-HMDI-HEMA content in the (co)polymers was 0 mol % (black squares), 2.5 mol % (red circles), 5 mol % (blue triangles), and 10 mol % (green diamonds).

fact, that in the case of the copolymer with 10 mol % UPy-HMDI-HEMA, E is much lower than E' established by DMA (82 vs 600 MPa), is likely related to the latter effect, as small variations in temperature or frequency (as is the case when DMA and tensile test data are compared) can have a significant influence on the modulus.

The poly(butyl-MA) series displays stress−strain curves that are characteristic of ductile and brittle plastics.[56−58] The neat polymer shows an elastic behavior below 4% strain, before necking is observed and the sample fails at ε^b of 60% and σ^b of 8 MPa. Table 4 shows that E increases upon incorporation of UPy-HMDI-HEMA from 640 (neat polymer) to 1640 MPa, whereas ε^b is gradually reduced to reach 0.3% in the case of the 10 mol % UPy containing copolymer. The maximum stress σ^b, always displayed at the point of necking ($\varepsilon(\sigma^{\max})$), remains largely unchanged around 14 MPa up to a UPy-HMDI-HEMA content of 5 mol %, but drops to around 5 MPa upon introduction of additional cross-linker. Together with the low ε^b and U_t values, this reflects the high brittleness of the 10 mol % UPy containing poly(UPy-HMDI-HEMA-*co*-butyl-MA).

Table 4. Mechanical Data of Poly(UPy-HMDI-HEMA-*co*-hexyl-MA) and Poly(UPy-HMDI-HEMA-*co*-butyl-MA) Determined by Stress−Strain Measurements at 24 ± 1 °C^a

UPy (mol %)	ε^b (%)	σ^b (MPa)	E (MPa)	$\varepsilon(\sigma^{max})$ (%)	σ^{max} (MPa)	U_t (J/m^3 10^4)
poly(UPy-HMDI-HEMA-*co*-hexyl-MA)						
0	570 ± 20	1.9 ± 0.1	5.2 ± 0.3	566 ± 20	1.9 ± 0.1	600 ± 40
2.5	330 ± 80	1.9 ± 0.2	7.4 ± 1.6	290 ± 40	1.9 ± 0.3	390 ± 140
5	230 ± 40	2.8 ± 0.2	7.7 ± 5.1	225 ± 36	2.8 ± 0.2	460 ± 130
10	100 ± 20	5.8 ± 0.6	82 ± 15	101 ± 17	5.8 ± 0.6	400 ± 90
poly(UPy-HMDI-HEMA-*co*-butyl-MA)						
0	60 ± 10	8.0 ± 1.6	640 ± 50	4.22 ± 0.34	13.4 ± 0.5	620 ± 140
2.5	40 ± 5	3.4 ± 0.2	650 ± 90	3.76 ± 0.28	14.2 ± 0.4	330 ± 80
5	4.7 ± 2.0	14.7 ± 0.8	850 ± 310	3.05 ± 1.31	15.7 ± 1.8	60 ± 30
10	0.3 ± 0.1	5.5 ± 1.4	1640 ± 220	0.30 ± 0.12	5.5 ± 1.4	1.0 ± 0.6

^{a}Values are averages of 3−5 measurements for each sample. Errors are standard deviations. ε^b, strain at break; σ^b, stress at break; E, Young's modulus; $\varepsilon(\sigma^{max})$, strain at maximum stress; σ^{max}, maximum stress; U_t, (tensile) toughness.

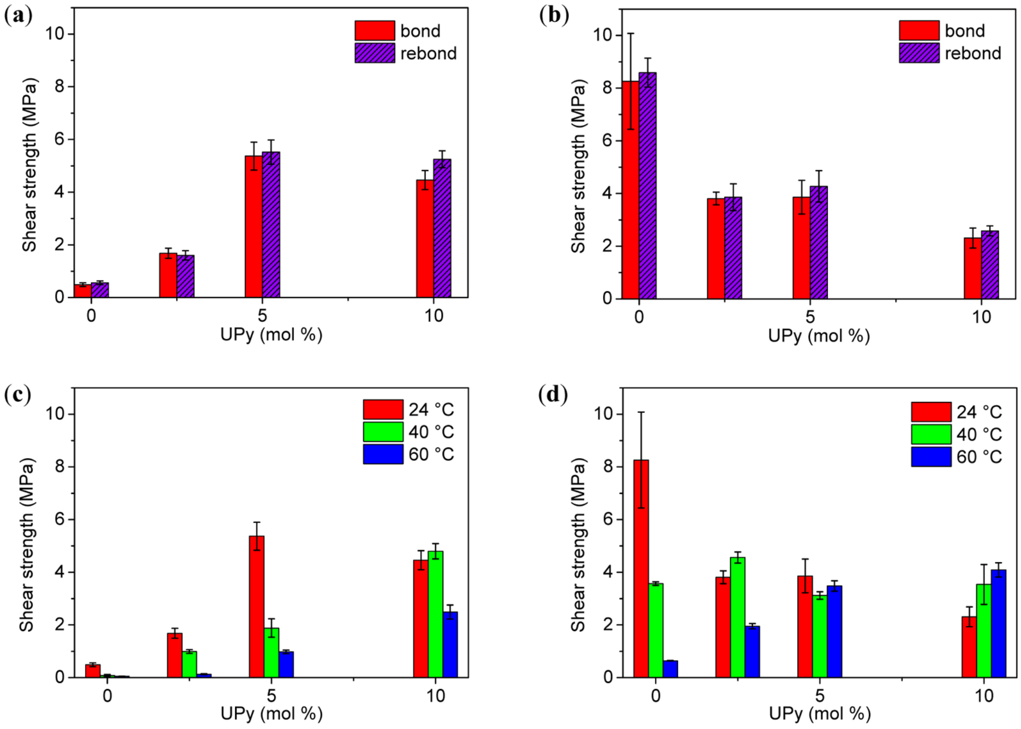


Figure 4. Shear strength of lap joints bonded with poly(UPy-HMDI-HEMA-*co*-hexyl-MA) (a, c) or poly(UPy-HMDI-HEMA-*co*-butyl-MA) (b, d). Graphs a and b display the initial shear strength (bond, red), and the shear strength of rebonded samples (rebond, purple) at room temperature. Graphs c and d show the initial shear strength as a function of temperature: 24 °C (red), 40 °C (green), and 60 °C (blue). Results are averages of 3−5 samples, and error bars are standard deviations. Rebonded samples were made by rebonding samples after they had been broken in an initial shear test experiment.

To explore the usefulness of the UPy-containing copolymers as stimuli-responsive reversible adhesives, single lap joints with an overlap area of 10 × 10 mm were prepared by sandwiching films of the supramolecular polymers with thickness of *ca.* 100 μm between two stainless steel substrates, and bonding these assemblies by heating to 140 °C in the case of the poly(butyl methacrylate) (co)polymers or 80−120 °C in the case of the poly(hexyl methacrylate) (co)polymers. The adhesion properties were then investigated at different temperatures by shear tests at a strain rate of 1 mm/min. The data thus collected are displayed in Figure 4 and Table 5. In the case of poly(UPy-HMDI-HEMA-*co*-hexyl-MA), a significant increase of the adhesive strength can be observed with increasing UPy concentration. At 24 °C, the effect levels off at a UPy content of 5 mol %, with a shear strength that is 10-fold higher than that of the poly(hexyl-MA) homopolymer, whereas an increase of the UPy content to 10 mol % UPy has no further effect (Table 5, Figure 4a,c). At 40 and 60 °C, the shear strength increases more or less linearly with the UPy content over all concentrations tested. These trends can be explained by considering the phase behavior of the polymers and the relative importance of the supramolecular cross-links. The DSC and DMA experiments show that at the test temperature of 24 °C the poly(hexyl-MA) homopolymer and the 2.5 and 5 mol % UPy containing copolymers are all above their T_g (considering DSC; Table 2) and softening point (onset of the decrease of E'; Supporting Information Table S1), whereas the copolymer with 10 mol % UPy is within the glass transition. Thus, in the glassy state, the UPy cross-links do not exert a significant influence on the mechanical and adhesive characteristics, where brittle failure

Table 5. Shear Strength of Lap Joints Bonded with Poly(UPy-HMDI-HEMA-*co*-hexyl-MA) or Poly(UPy-HMDI-HEMA-*co*-butyl-MA)[a]

	shear strength (MPa)			
UPy (mol %)	24 °C	24 °C (rebonded)	40 °C	60 °C
poly(UPy-HMDI-HEMA-*co*-hexyl-MA)				
0	0.5 ± 0.1	0.7 ± 0.1	0.1 ± 0.04	0.05 ± 0.01
2.5	1.7 ± 0.2	1.6 ± 0.2	1.0 ± 0.1	0.13 ± 0.02
5	5.4 ± 0.5	5.5 ± 0.5	1.9 ± 0.4	1.0 ± 0.1
10	4.5 ± 0.4	5.3 ± 0.3	4.8 ± 0.3	2.5 ± 0.3
poly(UPy-HMDI-HEMA-*co*-butyl-MA)				
0	8.3 ± 1.8	8.6 ± 0.6	3.6 ± 0.1	0.64 ± 0.01
2.5	3.8 ± 0.2	3.9 ± 0.5	4.6 ± 0.2	2.0 ± 0.1
5	3.9 ± 0.6	4.3 ± 0.6	3.1 ± 0.1	3.5 ± 0.2
10	2.6 ± 0.2	2.6 ± 0.2	3.7 ± 0.8	4.1 ± 0.3

[a] Shear strength measured for single lap joints made with stainless steel substrates. Results are averages of 3−5 measurements, and errors are standard deviations.

dominates, whereas in the rubbery state, a higher cross-link density not only leads to an increase of tensile strength and stiffness, but also higher adhesive strength, presumably on account of reducing creep, comparable to covalently cross-linked acrylic adhesives (*vide infra*).[59] Accordingly, the adhesion measurements conducted at 40 or 60 °C show an improvement of the adhesive strength when the UPy concentration is increased from 5 to 10 mol %.

The conclusion that the reduction of creep by the UPy cross-links leads to improved bonding at elevated temperatures is also supported by the failure modes observed for the lap joints after shear tests (Supporting Information Figure S12). Lap joints bonded with hexyl-MA homopolymer showed delamination/adhesive failure.[60] The origin of this failure mechanism (*viz-a-viz* cohesive failure) is the high elongation at break and high toughness of this material (Table 4), which are the highest for all tested materials. With increasing UPy concentration, an increasing cohesive component to the failure mode can be observed, which is probably associated with the decreasing elongation at break (Figure 3, Table 4). Possibly, the adhesion to the metal surface is also increased with increasing UPy concentration due to the polar nature of the UPy motif, which may provide better interactions with the metal surface. At elevated temperatures (40 and 60 °C), the mechanical properties of the hexyl-MA homopolymer deteriorate increasingly due to the absence of cross-links, leading to entirely cohesive failure (creep), whereas the cross-linked poly(UPy-HMDI-HEMA-*co*-hexyl-MA) copolymers are all rubbery. The 2.5 mol % UPy copolymer has a T_{fail} of 75 °C (Table 3), which is close to the test temperature of 60 °C, and therefore displays largely cohesive failure, in contrast to the copolymers containing 5 or 10 mol % UPy, which exhibit a T_{fail} of *ca.* 125 °C and consequently display mainly adhesive failure.

A more complex behavior is observed for poly(UPy-HMDI-HEMA-*co*-butyl-MA), where at 24 °C the highest adhesive strength was found for the poly(butyl-MA) homopolymer. At this temperature, the introduction of UPy-HMDI-HEMA caused a reduction of the shear strength by a factor of up to

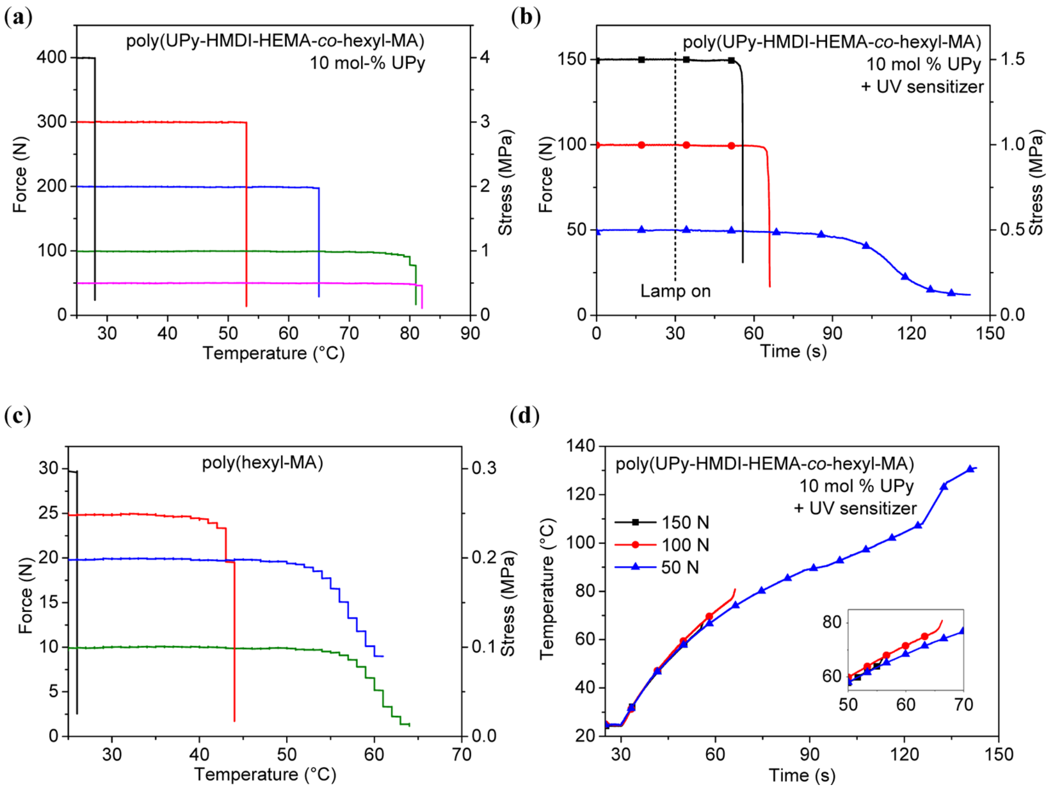


Figure 5. Debond on demand experiments with 10 mol % UPy poly(UPy-HMDI-HEMA-*co*-hexyl-MA) (a, b, d) and poly(hexyl-MA) (c) at different forces. The debond stimulus was heat (heating rate: 5 °C/min) (a, c) or UV light (λ = 320−500 nm; power density = 2500 mW/cm^2) (b, d). For the UV experiments, 0.25 wt % of a UV sensitizer was incorporated in the polymer. The corresponding debonding temperature of experiment (b) was measured with an IR camera and is depicted in (d).

3 for the 10 mol % UPy copolymer (Table 5, Figure 4b,d). This trend is reversed as the temperature is increased. At 40 °C, the adhesive strength is largely independent of the UPy content, whereas at 60 °C a gradual increase of the shear strength from 0.6 MPa (homopolymer) to 4.1 MPa (10 mol % UPy) is seen. Also in this case, the adhesive characteristics are well correlated with the phase behavior and cross-link density. At 24 °C, the UPy-containing poly(UPy-HMDI-HEMA-*co*-butyl-MA) copolymers are all glassy and brittle, whereas the butyl-MA homopolymer is just transitioning from the glassy to the rubbery state (Figure 2, Table 2). As for poly(hexyl-MA), the adhesive strength of poly(butyl-MA) decreases upon increasing the temperature. On the other hand, at 40 °C, the UPy-containing copolymers remain glassy, and their adhesive properties are comparable to those at 24 °C. At 60 °C the 2.5 and 5 mol % UPy containing copolymers are above T_g, where the material properties are dependent on the cross-link density, whereas the 10 mol % UPy containing copolymer is just approaching T_g, and thus displays adhesive properties that are the same as at 40 °C.

Also in the case of the poly(UPy-HMDI-HEMA-*co*-butyl-MA) (co)polymers, the interpretation of the temperature-dependent adhesion properties are supported by the failure mode (Supporting Information Figure S13). At 24 °C, the (co)polymers show adhesive (brittle) failure, whereas at higher temperatures, the failure mode is a mix of cohesive and adhesive failure, with the exception of the poly(butyl-MA) homopolymer at 60 °C, which shows predominantly creeping failure. The mix of cohesive and adhesive failure at higher temperatures can be explained by the fact that the materials are shifted toward the rubbery regime and become less brittle. On the basis of the similarity of the trends seen for the two (co)polymer series, one can speculate that adhesive failure should be dominating if the temperature was increased further.

All of the materials investigated here permit debonding on demand, as well as subsequent rebonding. Quantitative rebonding experiments, in which lap joints that had been debonded during shear-testing were rebonded using the original bonding conditions, show that the rebonded lap joints display a shear strength that is indistinguishable from that of the original bond (Table 5, Figure 4a,b).

We further exemplarily explored the debonding on demand feature for the 10 mol % UPy containing poly(UPy-HMDI-HEMA-*co*-hexyl-MA) (Figure 5a). When subjected to heat, debonding of lap joints occurred at *ca.* 80 °C at low forces (50 and 100 N), but the debonding temperature was reduced when higher forces were applied. As a reference experiment, a similar debonding experiment was carried out with poly(hexyl-MA), in which case debonding occurred at lower forces (30 N at the lowest temperature, Figure 5c). The failure mechanisms of UPy-functionalized and nonfunctionalized poly(hexyl-MA) were also investigated (Supporting Information Figures S14 and S15). At high forces, lower temperatures are necessary to debond, in which case mainly adhesive failure is observed. By contrast, low forces require higher temperatures for debonding, and support cohesive failure. Additionally, the temperature range in which debonding occurs is narrower over a higher temperature range in the case of the 10 mol % UPy poly(UPy-HMDI-HEMA-*co*-hexyl-MA) compared to poly(hexyl-MA) (Figure 5a,c). Although the absorbance of the copolymer is not sufficiently high to permit light-induced heating, this feature, which permits (de)bonding with light, could be enabled by introducing a small amount (0.25 wt %) of the ultraviolet light absorber 2-(5-chloro-2H-benzotriazole-2-yl)-6-(1,1-dimethylethyl)-4-methyl-phenol (Tinuvin 326), as previously reported.[35] This compound displays absorption maxima at 311 and 348 nm (Supporting Information Figure S16), and can convert absorbed UV light into heat on account of radiationless decay.[61] Thus, when blend films of poly(UPy-HMDI-HEMA-*co*-hexyl-MA) and the UV-absorber were irradiated with UV light (λ = 320−500 nm, 2500 mW/cm^2), the temperature rose to the decomposition temperature of 258 °C within seconds (Supporting Information Figure S17). When the polymer film was attached onto, or placed between quartz slides, the substrate acted as a heat sink, and a decreased heating rate was observed.

To permit optical stimulation, we fabricated lap joints based on quartz slides that were thermally bonded with the light sensitive formulation or, alternatively, bonded by illumination with ultraviolet light (λ = 320−500 nm, 2500 mW/cm^2, 2 × 40 s). Although the visual inspection of these samples suggests intimate bonding (Supporting Information Figure S18), a quantitative evaluation of the resulting bonding strength was not possible, as the quartz substrates broke before the bond failed, due to the lower mechanical stability of quartz glass compared to steel. When lap joints bonded with the UV-absorber containing 10 mol % UPy poly(UPy-HMDI-HEMA-*co*-hexyl-MA) were irradiated with UV light (λ = 320−500 nm, 2500 mW/cm^2) to achieve debonding, separation was achieved after 25, 35, or *ca.* 95 s with loads of 150, 100, or 50 N, respectively (Figure 5b). The corresponding debonding temperatures are *ca.* 65, 77, and 108 °C, respectively, and were recorded in parallel with an IR camera (Figure 5d). The failure mechanism was also investigated (Supporting Information Figure S19) and revealed increasing cohesive failure with decreasing applied forces due to the higher required debonding temperatures. A comparison shows that the debonding temperatures for thermally and optically induced debonding are largely comparable, with small differences that are likely related to the significant difference of the heating rates in the two processes.

CONCLUSIONS

We have shown here that the introduction of UPy side chains into poly(alkyl methacrylate)s affords copolymers in which the supramolecular cross-links formed through UPy dimerization significantly improves the adhesion in the rubbery state, and permit good adhesion over a large temperature range, whereas the UPy-free homopolymers rapidly fail upon heating to temperatures much higher than T_g. In this regime, the adhesive properties are comparable with those of commercially available hot-melt adhesives for household applications for bonding glass, wood and plastics.[62] As a result of the supramolecular nature of the cross-links, the materials can be rebonded and permit (de)bonding on demand, using either light or heat. Due to the great versatility of free radical polymerization, it appears to be straightforward to further tailor the properties of the materials at hand. Low-T_g supramolecular polymer networks appear to be useful as pressure-sensitive adhesives (PSA), as the reversible cross-linking should increase creep-resistance,[63,64] but at the same time permit easy removal upon thermal dissociation.[65] High-T_g supramolecular polymer networks exhibit similar debonding-on-demand capabilities, but offer mechanical characteristics that are closer to those of thermoset resins than PSAs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic details and characterization by NMR, DSC, and TGA; submersion-DMA data; pictures of adhesive experiments and their failure mode; UV−vis absorption spectra; temperature−time-diagram for UV light irradiated polymer films; pictures of optically and thermally bonded samples; failure mode investigations after debond on demand experiments. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b01939.

■ AUTHOR INFORMATION

Corresponding Author

*C. Weder. E-mail: christoph.weder@unifr.ch.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Commission for Technology and Innovation (CTI, Grant No. 13746.1), the Ivoclar Vivadent AG, and the Adolphe Merkle Foundation for support of this research.

■ REFERENCES

(1) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. Supramolecular Polymers. *Chem. Rev.* **2001**, *101*, 4071−4097.

(2) Lawrence, D. S.; Jiang, T.; Levett, M. Self-Assembling Supramolecular Complexes. *Chem. Rev.* **1995**, *95*, 2229−2260.

(3) Huang, F.; Scherman, O. A. Supramolecular Polymers. *Chem. Soc. Rev.* **2012**, *41*, 5879−5880.

(4) Bosman, A. W.; Sijbesma, R. P.; Meijer, E. W. Supramolecular Polymers at Work. *Mater. Today* **2004**, *7*, 34−39.

(5) Lehn, J.-M. Dynamers: Dynamic Molecular and Supramolecular Polymers. *Prog. Polym. Sci.* **2005**, *30*, 814−831.

(6) Kumpfer, J. R.; Rowan, S. J. Thermo-, Photo-, and Chemo-Responsive Shape-Memory Properties from Photo-Cross-Linked Metallo-Supramolecular Polymers. *J. Am. Chem. Soc.* **2011**, *133*, 12866−12874.

(7) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Ky Hirschberg, J. H. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. Reversible Polymers Formed from Self-Complementary Monomers Using Quadruple Hydrogen Bonding. *Science* **1997**, *278*, 1601−1604.

(8) Ma, X.; Tian, H. Stimuli-Responsive Supramolecular Polymers in Aqueous Solution. *Acc. Chem. Res.* **2014**, *47*, 1971−1981.

(9) Jochum, F. D.; Theato, P. Temperature- and Light-Responsive Smart Polymer Materials. *Chem. Soc. Rev.* **2013**, *42*, 7468−7483.

(10) 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.

(11) 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.* **2012**, *1*, 204−208.

(12) Bu, J.; Lilienthal, N. D.; Woods, J. E.; Nohrden, C. E.; Hoang, K. T.; Truong, D.; Smith, D. K. Electrochemically Controlled Hydrogen Bonding. Nitrobenzenes as Simple Redox-Dependent Receptors for Arylureas. *J. Am. Chem. Soc.* **2005**, *127*, 6423−6429.

(13) Nakahata, M.; Takashima, Y.; Yamaguchi, H.; Harada, A. Redox-Responsive Self-Healing Materials formed from Host-Guest Polymers. *Nat. Commun.* **2011**, *2*, 1521/1−1521/6.

(14) Beijer, F. H.; Sijbesma, R. P.; Kooijman, H.; Spek, A. L.; Meijer, E. W. Strong Dimerization of Ureidopyrimidones via Quadruple Hydrogen Bonding. *J. Am. Chem. Soc.* **1998**, *120*, 6761−6769.

(15) 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.

(16) Nieuwenhuizen, M. M. L.; de Greef, T. F. A.; van der Bruggen, R. L. J.; Paulusse, J. M. J.; Appel, W. P. J.; Smulders, M. M. J.; Sijbesma, R. P.; Meijer, E. W. Self-Assembly of Ureido-Pyrimidinone Dimers into One-Dimensional Stacks by Lateral Hydrogen Bonding. *Chem.—Eur. J.* **2010**, *16*, 1601−1612.

(17) Biyani, M. V.; Foster, E. J.; Weder, C. Light-Healable Supramolecular Nanocomposites Based on Modified Cellulose Nanocrystals. *ACS Macro Lett.* **2013**, *2*, 236−240.

(18) Coulibaly, S.; Heinzmann, C.; Beyer, F. L.; Balog, S.; Weder, C.; Fiore, G. L. Supramolecular Polymers with Orthogonal Functionality. *Macromolecules* **2014**, *47*, 8487−8496.

(19) Chen, Y.; Jones, S. T.; Hancox, I.; Beanland, R.; Tunnah, E. J.; Bon, S. A. F. Multiple Hydrogen-Bond Array Reinforced Cellular Polymer Films from Colloidal Crystalline Assemblies of Soft Latex Particles. *ACS Macro Lett.* **2012**, *1*, 603−608.

(20) Kuo, S.-W.; Tsai, H.-T. Self-Complementary Multiple Hydrogen Bonding Interactions Increase the Glass Transition Temperatures to Supramolecular Poly(methyl methacrylate) Copolymers. *J. Appl. Polym. Sci.* **2012**, *123*, 3275−3282.

(21) Lewis, C. L.; Stewart, K.; Anthamatten, M. The Influence of Hydrogen Bonding Side-Groups on Viscoelastic Behavior of Linear and Network Polymers. *Macromolecules* **2014**, *47*, 729−740.

(22) Yamauchi, K.; Lizotte, J. R.; Long, T. E. Thermoreversible Poly(alkyl acrylates) Consisting of Self-Complimentary Multiple Hydrogen Bonding. *Macromolecules* **2003**, *36*, 1083−1088.

(23) 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.

(24) Söntjens, S. H. M.; Renken, R. A. E.; van Gemert, G. M. L.; Engels, T. A. P.; Bosman, A. W.; Janssen, H. M.; Govaert, L. E.; Baaijens, F. P. T. Thermoplastic Elastomers Based on Strong and Well-Defined Hydrogen-Bonding Interactions. *Macromolecules* **2008**, *41*, 5703−5708.

(25) Wei, M.; Zhan, M.; Yu, D.; Xie, H.; He, M.; Yang, K.; Wang, Y. Novel Poly(tetramethylene ether)Glycol and Poly(ε-caprolactone) based Dynamic Network via Quadruple Hydrogen Bonding with Triple-Shape Effect and Self-Healing Capacity. *ACS Appl. Mater. Interfaces* **2015**, *7*, 2585−2596.

(26) Hoorne-van Gemert, G. M. L.; Janssen, H. M.; Meijer, E. W.; Bosman, A. W. Supramolecular Polymers from Low-Melting, Easily Processable Building Blocks. WO 2008063057 A2, May 05, 2008.

(27) Hoorne-van Gemert, G. M. L.; Chodorowski-Kimmès, S.; Janssen, H. M.; Meijer, E. W.; Bosman, A. W. High Flow Supramolecular Compounds. WO 2010/002262 A1, July 1, 2010.

(28) 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.

(29) Hoogenboom, R. Hard Autonomous Self-Healing Supramolecular Materials - A Contradiction in Terms? *Angew. Chem., Int. Ed.* **2012**, *51*, 11942−11944.

(30) Li, J.; Viveros, J. A.; Wrue, M. H.; Anthamatten, M. Shape-Memory Effects in Polymer Networks Containing Reversibly Associating Side-Groups. *Adv. Mater.* **2007**, *19*, 2851−2855.

(31) Wang, R.; Xie, T. Shape Memory- and Hydrogen Bonding-based Strong Reversible Adhesive System. *Langmuir* **2010**, *26*, 2999−3002.

(32) Ware, T.; Hearon, K.; Lonnecker, A.; Wooley, K. L.; Maitland, D. J.; Voit, W. Triple-Shape Memory Polymers Based on Self-Complementary Hydrogen Bonding. *Macromolecules* **2012**, *45*, 1062−1069.

(33) Zhang, H.; Chen, Y.; Lin, Y.; Fang, X.; Xu, Y.; Ruan, Y.; Weng, W. Spiropyran as a Mechanochromic Probe in Dual Cross-Linked Elastomers. *Macromolecules* **2014**, *47*, 6783−6790.

(34) Teunissen, A. J. P.; Nieuwenhuizen, M. M. L.; Rodríguez-Llansola, F.; Palmans, A. R. A.; Meijer, E. W. Mechanically Induced Gelation of a Kinetically Trapped Supramolecular Polymer. *Macromolecules* **2014**, *47*, 8429−8436.

(35) Heinzmann, C.; Coulibaly, S.; Roulin, A.; Fiore, G. L.; Weder, C. Light-Induced Bonding and Debonding with Supramolecular Adhesives. *ACS Appl. Mater. Interfaces* **2014**, *6*, 4713−4719.

(36) Luo, X.; Lauber, K. E.; Mather, P. T. A Thermally Responsive, Rigid, and Reversible Adhesive. *Polymer* **2010**, *51*, 1169−1175.

(37) de Greef, T. F. A.; Smulders, M. M. J.; Wolffs, M.; Schenning, A. P. H. J.; Sijbesma, R. P.; Meijer, E. W. Supramolecular Polymerization. *Chem. Rev.* **2009**, *109*, 5687−5754.

(38) Feldman, K. E.; Kade, M. J.; de Greef, T. F. A.; Meijer, E. W.; Kramer, E. J.; Hawker, C. J. Polymers with Multiple Hydrogen-Bonded End Groups and Their Blends. *Macromolecules* **2008**, *41*, 4694−4700.

(39) Appel, W. P. J.; Portale, G.; Wisse, E.; Dankers, P. Y. W.; Meijer, E. W. Aggregation of Ureido-Pyrimidinone Supramolecular Thermoplastic Elastomers into Nanofibers: A Kinetic Analysis. *Macromolecules* **2011**, *44*, 6776−6784.

(40) Faghihnejad, A.; Feldman, K. E.; Yu, J.; Tirrell, M. V.; Israelachvili, J. N.; Hawker, C. J.; Kramer, E. J.; Zeng, H. Adhesion and Surface Interactions of a Self-Healing Polymer with Multiple Hydrogen-Bonding Groups. *Adv. Funct. Mater.* **2014**, *24*, 2322−2333.

(41) Hosono, N.; Gillissen, M. A.; Li, Y.; Sheiko, S. S.; Palmans, A. R.; Meijer, E. W. Orthogonal Self-Assembly in Folding Block Copolymers. *J. Am. Chem. Soc.* **2013**, *135*, 501−510.

(42) Foster, E. J.; Berda, E. B.; Meijer, E. W. Metastable Supramolecular Polymer Nanoparticles via Intramolecular Collapse of Single Polymer Chains. *J. Am. Chem. Soc.* **2009**, *131*, 6964−6966.

(43) Park, T.; Zimmermann, S. C. Interplay of Fidelity, Binding Strength, and Structure in Supramolecular Polymers. *J. Am. Chem. Soc.* **2006**, *79*, 14236−14237.

(44) Feldman, K. E.; Kade, M. J.; Meijer, E. W.; Hawker, C. J.; Kramer, E. J. Model Transient Networks from Strongly Hydrogen-Bonded Polymers. *Macromolecules* **2009**, *42*, 9072−9081.

(45) Cashion, M.; Park, T.; Long, T. Influence of Hydrogen Bonding on the Adhesive Properties of Photo-Curable Acrylics. *J. Adhes.* **2009**, *85*, 1−17.

(46) 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.

(47) Chabert, F.; Tournilhac, F.; Sajot, N.; Tencé-Girault, S.; Leibler, L. Supramolecular Polymer for Enhancement of Adhesion and Processability of Hot Melt Polyamides. *Int. J. Adhes. Adhes.* **2010**, *30*, 696−705.

(48) Ahn, Y.; Jang, Y.; Selvapalam, N.; Yun, G.; Kim, K. Supramolecular Velcro for Reversible Underwater Adhesion. *Angew. Chem., Int. Ed.* **2013**, *52*, 3140−3144.

(49) Berda, E. B.; Foster, E. J.; Meijer, E. W. Toward Controlling Folding in Synthetic Polymers: Fabricating and Characterizing Supramolecular Single-Chain Nanoparticles. *Macromolecules* **2010**, *43*, 1430−1437.

(50) Cheng, S.; Zhang, M.; Dixit, N.; Moore, R. B.; Long, T. E. Nucleobase Self-Assembly in Supramolecular Adhesives. *Macromolecules* **2012**, *45*, 805−812.

(51) Brazel, C. S.; Peppas, N. A. Synthesis and Characterization of Thermo- and Chemomechanically Responsive Poly(N-isopropylacrylamide-co-methacrylic acid) Hydrogels. *Macromolecules* **1995**, *28*, 8016−8020.

(52) Hao, J.; Weiss, R. A. Viscoelastic and Mechanical Behavior of Hydrophobically Modified Hydrogels. *Macromolecules* **2011**, *44*, 9390−9398.

(53) Bermejo, J. S.; Ugarte, C. M. Influence of Cross-Linking Density on the Glass Transition and Structure of Chemically Cross-Linked PVA: A Molecular Dynamics Study. *Macromol. Theory Simul.* **2009**, *18*, 317−327.

(54) Salgueiro, W.; Marzocca, A.; Somoza, A.; Consolati, G.; Cerveny, S.; Quasso, F.; Goyanes, S. Dependence of the Network Structure of Cured Styrene Butadiene Rubber on the Sulphur Content. *Polymer* **2004**, *45*, 6037−6044.

(55) Hutin, M.; Burakowska-Meise, E.; Appel, W. P. J.; Dankers, P. Y. W.; Meijer, E. W. From Molecular Structure to Macromolecular Organization: Keys to Design Supramolecular Biomaterials. *Macromolecules* **2013**, *46*, 8528−8537.

(56) Bueche, F. Tensile Strength of Plastics above the Glass Temperature. *J. Appl. Phys.* **1955**, *26*, 1133−1140.

(57) Blond, D.; Barron, V.; Ruether, M.; Ryan, K. P.; Nicolosi, V.; Blau, W. J.; Coleman, J. N. Enhancement of Modulus, Strength, and Toughness in Poly(methyl methacrylate)-based Composites by the Incorporation of Poly(methyl methacrylate)-Functionalized Nanotubes. *Adv. Funct. Mater.* **2006**, *16*, 1608−1614.

(58) Balkan, O.; Demirer, H. Mechanical Properties of Glass Bead- and Wollastonite-Filled Isotactic-Polypropylene Composites Modified with Thermoplastic Elastomers. *Polym. Compos.* **2010**, *31*, 1285−1308.

(59) Sosson, F.; Chateauminois, A.; Creton, C. Investigation of Shear Failure Mechanisms of Pressure-Sensitive Adhesives. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 3316−3330.

(60) Cherian, Z.; Lehman, R. Effects of Adhesive Type and Polystyrene Concentration on the Shear Strength of Bonded Polystyrene/High-Density Polyethylene Blends. *Int. J. Adhes. Adhes.* **2005**, *25*, 502−506.

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

(62) Swan, D. G.; Hansen, J. C. Poly(ester-amide) composition. EP 0204315 A2, December 10, 1986.

(63) Tobing, S. D.; Klein, A. Molecular Parameters and Their Relation to the Adhesive Performance of Acrylic Pressure-Sensitive Adhesives. *J. Appl. Polym. Sci.* **2001**, *79*, 2230−2244.

(64) Creton, C. Pressure-Sensitive Adhesives: An Introductory Course. *MRS Bull.* **2003**, *28*, 434−439.

(65) Inui, T.; Sato, E.; Matsumoto, A. Pressure-Sensitive Adhesion System Using Acrylate Block Copolymers in Response to Photoirradiation and Postbaking as the Dual External Stimuli for On-Demand Dismantling. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2124−2132.