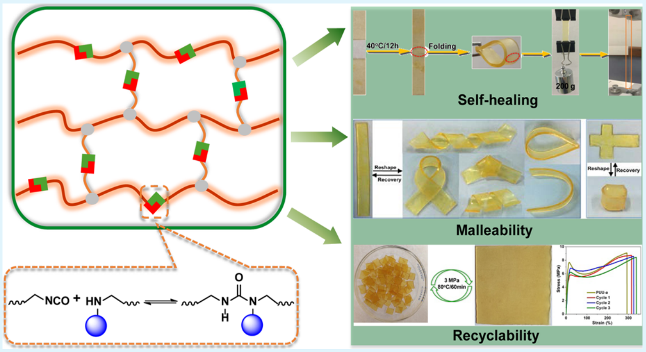
ACS APPLIED MATERIALS & INTERFACES

www.acsami.org Research Article

Recyclable, Self-Healable, and Highly Malleable Poly(urethane-urea)s with Improved Thermal and Mechanical Performances

Shujuan Wang,*,⊥ Yingfeng Yang,⊥ Hanze Ying, Xinli Jing, Bin Wang, Yanfeng Zhang, and Jianjun Cheng*

Cite This: *ACS Appl. Mater. Interfaces* 2020, 12, 35403−35414 Read Online



ABSTRACT: Developing recyclable, self-healable, and highly malleable thermosets is one of the keys to relieve environmental pollution and meet our increasing demand for "greener" materials. Hindered urea bonds (HUBs) have been successfully incorporated in preparing dynamic covalent networks with those desirable properties. However, one key drawback is the low thermal stability and poor mechanical performance of previously reported systems. In this work, we demonstrated that the incorporation of aromatic moiety-containing diamine-based HUBs can greatly improve the thermal and mechanical performance of the poly(urethane-urea)s (PUUs) while still maintaining the desirable recycling, self-healing, and reprocessing properties. Studies on model compounds revealed the origin of the thermal stability and demonstrated the dynamic property. The aromatic-containing diamine-based HUBs were then used to prepare a series of catalyst-free PUUs with improved thermal and mechanical properties. The dynamic HUBs significantly reduced the relaxation timescale and allowed the PUU networks to be recycled multiple times. The healed and recycled PUUs regained most of the mechanical strength and integrity of the original material. Therefore, this unique and simple approach is expected to open up new avenues to design PUUs with optimal performance for various applications.

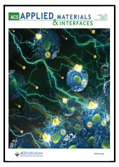
KEYWORDS: *poly(urethane-urea)s, hindered urea bonds, self-healing, recyclability, malleability*

■ INTRODUCTION

Due to their excellent dimensional stability, chemical resistance, and thermal and mechanical performances, thermosets are used in a wide range of applications, including structural composites, adhesives, coatings, and electrical insulation.[1] However, conventional thermosets cannot be reshaped, reprocessed, or recycled due to their inability to melt or flow at high temperatures.[2,3] In contrast, thermoplastics become moldable at high temperatures and can return to a solid state when cooled; such property enables facile processing and recycling of thermoplastics when heated.[4,5] An effective chemical strategy to combine these properties is to introduce dynamic chemical bonds into a polymer network, resulting in a dynamic polymer network.[6,7] Reversible covalent bonds can participate in reversible breakage and reformation under specific conditions or stimuli, which enables network rearrangement and endows them with dynamic properties (such as recyclability, shape memory, or self-healing).[8]

Polymers containing dynamic bonds are considered covalent adaptable networks (CANs), as proposed by Bowman and Kloxin.[9,10] A variety of dynamic covalent bonds have been explored to prepare reversible polymers, including disulfide exchange, transesterification, imine exchange, transcarbamoylation, Diels−Alder chemistry, alkoxyamine chemistry, or boronic ester exchange.[11−14] One type of CANs is based on the dissociative exchange mechanism (i.e., Diels−Alder reactions) in which the chemical bonds are first broken and then reformed at another location.[15] The temporary loss of cross-links leads to a sudden drop in viscosity; such materials can experience fast topology rearrangements because of a decrease in network integrity. For associative bond exchange mechanisms, covalent bonds are only destroyed when new ones are formed, resulting in a fixed cross-linking density with increasing temperature.[16] However, most of the current reversible systems involve the use of external stimuli (i.e., light, heat, electricity, or catalysts) to facilitate the association and dissociation reversion, which increases the complexity of recycling or large-scale production.[17,18] Additionally, they are limited by the availability of commercial raw materials and the

Received: April 24, 2020
Accepted: July 17, 2020
Published: July 17, 2020



https://dx.doi.org/10.1021/acsami.0c07553

number of procedures required for material fabrication.[19] Therefore, it is desirable to develop a new class of polymers that have reprocessability, remoldability, recyclability, and self-healing performance in the absence of catalysts.

Our previous study demonstrated that urea bonds bearing a bulky group on the nitrogen atom resulted in hindered urea bonds (HUBs) that were dynamic and can reversibly dissociate into an amine and isocyanate based on the associative exchange mechanisms.[20,21] Especially, the dynamic reversibility of HUBs can be flexibly tuned by adjusting the bulky substituents. Ever since its first report, HUBs have been widely used in preparing dynamic covalent networks with various adaptive properties, and among them most was *N*,*N*′-di-*tert*-butylethylenediamine (TBEA)-based poly(urethane-urea) (PUU-TBEA).[22] Despite of their reported excellent self-healing abilities at room temperature and shape memory properties, their poor mechanical strength (breaking stress: 0.93 MPa) greatly limits their application for various industrial uses.[23,24] Another issue with such a system is their poor thermal stability at high temperatures, which was often improved, however, at the cost of a reduced processability and chain mobility during dynamic healing.[25]

To deal with the problem mentioned above, the aromatic moiety-containing *N*,*N*′-di-*tert*-butyl-*p*-xylylenediamine (TBXA) was innovatively synthesized, and the recyclable, self-healable, and highly malleable TBXA-based PUUs with improved thermal and mechanical performances were synthesized. Generally, PUUs are prepared by changing soft and hard segments along the molecular chains. Hard segments with high glass-transition temperature (T_g) are prepared from the reaction of an isocyanate and amine, which tend to self-assemble into domains through physical cross-links, providing mechanical, thermal, and solvent-resistance to a material. Soft segments with low T_g are prepared from alkyl blocks, polyethers, or polyesters, which exhibit low-temperature flexibility and self-healing abilities under mild conditions. In this work, three fundamental principles were utilized to yield the PUU networks: (i) utilization of *m*-xylylenediisocyanate (XDI) and TBXA with aromatic rings to improve the thermal stability and mechanical robustness of the materials, (ii) incorporation of aromatic moiety-containing diamine TBXA to endow polymer networks with reprocessability, recyclability, and self-healing ability, and (iii) using poly(propylene glycol) (PPG) with a moderate molecular weight (M_n = 1000) as the soft segment to achieve sufficient mobility during healing. Varying the chain extender contents to tune the T_g and mechanical properties of PUUs leads to a great flexibility in tuning the topological rearrangement to allow reprocessing and self-healing over a wide temperature range.[26] A thorough study of the thermal and mechanical properties, recyclability, and self-healing ability of PUUs was conducted to determine the role of the aromatic-containing HUBs. It is especially important that the molecular design strategy is also applicable for other thermoset systems (such as epoxy resin).

■ EXPERIMENTAL SECTION

Materials. *N*-Benzyl-*tert*-butylamine, *tert*-butyl(ethyl)amine, PPG (M_n = 1000), tetraethylene glycol (TEG, M_n = 194), triethanolamine (TEA), 1,4-bis(bromomethyl)benzene, *tert*-butylamine, 1,4-phenylenedimethanamine, cesium carbonate (Cs_2CO_3), and anhydrous sodium sulfate (Na_2SO_4) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received unless otherwise specified. XDI (99%), TBEA (99%), hexamethylene diisocyanate (HDI, 99%), benzyl isocyanate, and butyl isocyanate were purchased from TCI America (Portland, OR, USA) and used as received. *N*-Methyl-2-pyrrolidone, tetrahydrofuran (THF), *N*,*N*-dimethylformamide, chloroform ($CHCl_3$, 99.8%), acetone, dichloromethane (DCM), ethyl acetate, and alcohol were purchased from Cambridge Isotope Laboratories, Inc. and used as received. Deionized water was made in our lab.

Synthesis of *N*,*N*′-di-*tert*-butyl-*p*-Xylylenediamine (TBXA). 1, 4-Bis(bromomethyl)benzene (10.83 g, 41 mmol) was dissolved in 150 mL of THF in a 500 mL three-neck, round-bottom flask under mechanical agitation. Then, *tert*-butyl amine (30.0 g, 410 mmol) and Cs_2CO_3 (13.36 g, 41 mmol) were added into the solution. The suspension was stirred at room temperature for about 3 days, and thin layer chromatography was used to verify the completion of the reaction. Then, the reaction was quenched with 200 mL of water and extracted with 900 mL of DCM. The organic layers were combined, washed twice with brine, and then dried over anhydrous Na_2SO_4. Finally, DCM was evaporated by a rotary evaporator to yield the white crystalline product in a 92% yield (Scheme S1). The structural characterization of TBXA is shown in Figures S1−S5.

Synthesis of Compound 1c. Benzyl isocyanate (**1a**, 133.2 mg, 1 mmol) and *N*,*N*′-di-*tert*-butylethylenediamine (**1b**, 124.2 mg, 0.5 mmol) were mixed in 10 mL of DCM. The mixture was stirred at room temperature for 30 min, and then solvent was removed. Compound **1c** was obtained as a white powder and used without purification (Scheme S2 and Figure S6).

Synthesis of Compound 2c. Benzyl isocyanate (**1a**, 133.2 mg, 1 mmol) and *N*-benzyl-*tert*-butylamine (**2b**, 163.3 mg, 1 mmol) were mixed in DCM (10 mL), and the mixture was stirred at room temperature for 30 min. The solvent was evaporated, and compound **2c** was obtained as a white powder and used without purification (Scheme S3 and Figure S7).

Synthesis of Compound 3c. Benzyl isocyanate (**1a**, 133.2 mg, 1 mmol) and **3b** (124.2 mg, 0.5 mmol) were mixed in 10 mL of DCM. The mixture was stirred at room temperature for 30 min, and then the solvent was evaporated. Compound **3c** was obtained as a white powder and used without purification (Scheme S4 and Figure S8).

Synthesis of Poly(2a/1b). Equal molar amounts of HDI (**2a**, 336.4 mg, 2 mmol) and TBEA (**1b**, 344.6 mg, 2 mmol) were dissolved in DCM (5.0 mL). The mixture was stirred at 37 °C for 2 h, and then poly(**2a**/**1b**) was formed (Scheme S5).

Synthesis of Poly(3a/1b). Equal molar amounts of *m*-xylylenediisocyanate (**3a**, 188.2 mg, 1 mmol) and TBEA (**1b**, 172.3 mg, 1 mmol) were dissolved in DCM (5.0 mL). The mixture was stirred at 37 °C for 2 h, and then poly(**3a**/**1b**) was formed (Scheme S6).

Synthesis of Poly(3a/3b). Equal molar amounts of *m*-xylylenediisocyanate (**3a**, 188.2 mg, 1 mmol) and TBXA (**3b**, 248.4 mg, 1 mmol) were added into DCM (2.0 mL). The mixture was stirred at 37 °C for 2 h and was analyzed by GPC to verify whether poly(**3a**/**3b**) was synthesized (Scheme S6).

Synthesis of HUB-Based PUUs. Using PUU-a as an example, the synthesis procedure was as follows: XDI (6.82 g, 36.3 mmol), TEA (0.40 g, 2.66 mmol), TEG (2.35 g, 12.1 mmol), PPG (3.02 g, 3.02 mmol), and $CHCl_3$ (50 mL) were magnetically stirred in a 100 mL double-neck round-bottom flask until a homogeneous mixture was obtained. After incubation at 60 °C for 2 h, a solution of TBXA (3 g, 12.1 mmol) in $CHCl_3$ was added dropwise into the flask to prevent excessive heating. Afterward, the dispersion was poured into a polytetrafluoroethylene mold. The curing process proceeded for 10 h in a vacuum drying oven at 60 °C until the disappearance of isocyanate absorption at 2238 cm^{-1} monitored by FTIR. A series of PUU samples, designated as PUU-a, PUU-b, PUU-c, and PUU-d were synthesized according to the molar ratio of the components in the PUUs (Table S1). PUU-e without dynamic HUBs was prepared as control through a similar procedure but using 1,4-phenylenedimethanamine as the diamine instead of TBXA. The TBEA-based PUU named as PUU-f was also prepared to facilitate the comparison of thermal and mechanical properties (Table S2).[23]

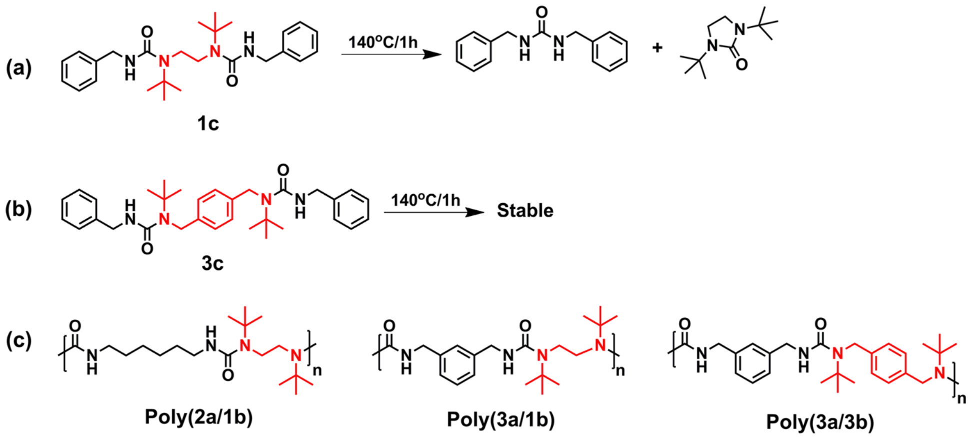


Figure 1. Schematic representation of model compounds (a) **1c**, (b) **3c**, and (c) linear poly(**2a**/**1b**), poly(**3a**/**1b**), and poly(**3a**/**3b**).

Characterization. Nuclear magnetic resonance (NMR) spectroscopy, gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), tensile mechanical tests, scratch-healing experiments, transmittance, stress−relaxation experiment, swelling experiment, and reprocessing and self-healing experiments were conducted, and the experimental details are summarized in the Supporting Information.

■ RESULTS AND DISCUSSION

Preliminary Studies and Project Design. Despite of their unique self-healing and multiple shape memory properties, previously reported TBEA-based PUUs suffer from low thermostability. The skeleton of cross-linked PUUs was degraded and some side reactions occurred at temperatures higher than 100 °C. To study their thermal degradation pathway, model compound **1c** was synthesized (Figure 1a and Scheme S2). After being incubated at 140 °C for 1 h, compound **1c** was degraded almost completely and structural analyses of the degradation products showed the formation of a stable urea compound and a five-membered cyclic urea, as evidenced by ^{1}H NMR and ESI-mass results (Figures S9 and S10). We postulated that the thermal degradation of TBEA-based PUUs was partially driven by the formation of the thermodynamically favorable five-membered ring. We envision that incorporation of rigid aromatic diamines instead of TBEA will block the formation of the five-membered cyclic structure and thus improve the thermal stability. Thus, TBXA was synthesized (Scheme S1) and chosen as a replacement of TBEA for ease of synthesis. As a proof of concept, model compound **3c** was synthesized and incubated at 140 °C for 1 h similar to **1c** (Figure 1b). Much to our delight, compounds **2c** and **3c** remained intact with little sign of degradation (Figures S11 and S12).

As a further support, linear poly(**2a**/**1b**), poly(**3a**/**1b**), and poly(**3a**/**3b**) were synthesized (Figure 1c), and TGA was conducted to compare their thermal stability. Generally, the thermal decomposition temperature at 5% weight loss (named as $T_{5\%}$) and char yield are widely used to assess the thermal stability.[27] The TGA and DTG curves of poly(**2a**/**1b**), poly(**3a**/**1b**), and poly(**3a**/**3b**) are presented in Figure S13 with the data summarized in Table S3. TGA indicated that poly(**3a**/**3b**) possessed the highest thermal decomposition temperature and char yield compared to poly(**2a**/**1b**) and poly(**3a**/**3b**), which were consistent with the ^{1}H NMR results of model compounds. For example, the $T_{5\%}$ and char yield of poly(**3a**/**3b**) at 450 °C were 215 °C and 22%, respectively, while those of poly(**3a**/**1b**) were 112 °C and 0, respectively. The results further demonstrated that introducing aromatic moiety-containing diamine was beneficial to the thermal stability of the HUB-based model compounds.

Dynamic Exchange Reactions of HUBs in Small Molecules and Polymers. Considering the fact that dynamic properties of the reversible cross-links play a crucial role in the properties of polymer networks, the dynamic exchange of this new HUB moiety in small molecules and linear polymers was first investigated. To evaluate the dynamic reversibility based on the new hindered diamine TBXA, its corresponding monomeric analog *N*-benzyl-*tert*-butylamine (**2b**) was selected and mixed with benzyl isocyanate (**1a**) in $CDCl_3$ giving **2c** bearing an HUB moiety. As expected, **2c** was reversible and demonstrated dynamic exchange with amine species **4b**, as evidenced by ^{1}H NMR analysis (Figure 2a and Figure S14).

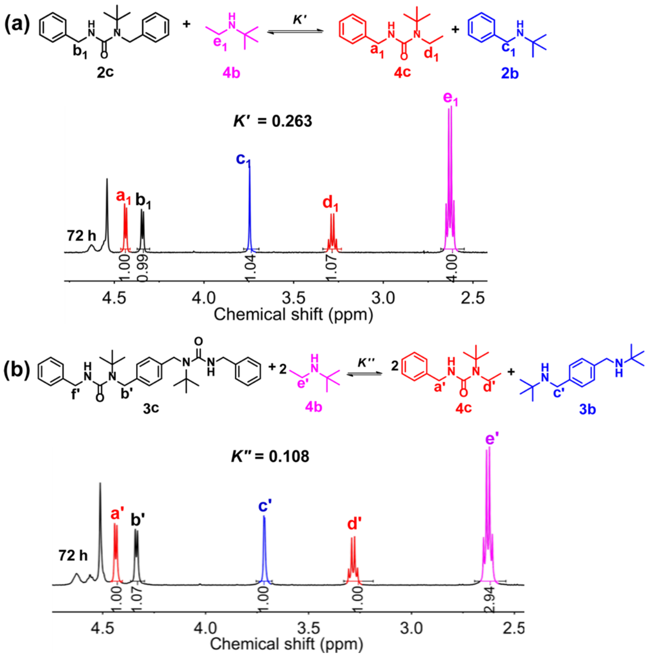


Figure 2. K' (a) and K'' (b) measurements of monoHUB and bisHUB based on the small-molecule model compound study of HUB exchange kinetics. ^{1}H NMR spectra were collected after mixing at 37 °C for 72 h until the reaction reached equilibrium.

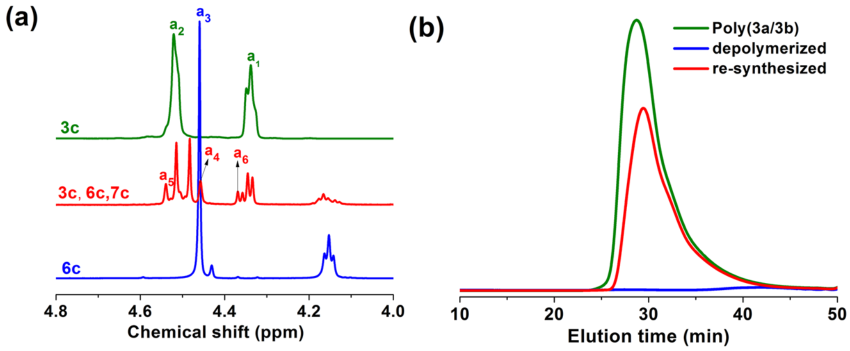


Figure 3. Dynamic properties of HUB-bearing small molecule or polymers. (a) ^{1}H NMR spectra of model compounds **3c** and **6c** and their 1:1 mixture after incubation at 37 °C for 48 h. (b) GPC analyses of the dynamic depolymerization and repolymerization of poly(**3a**/**3b**) in DCM.

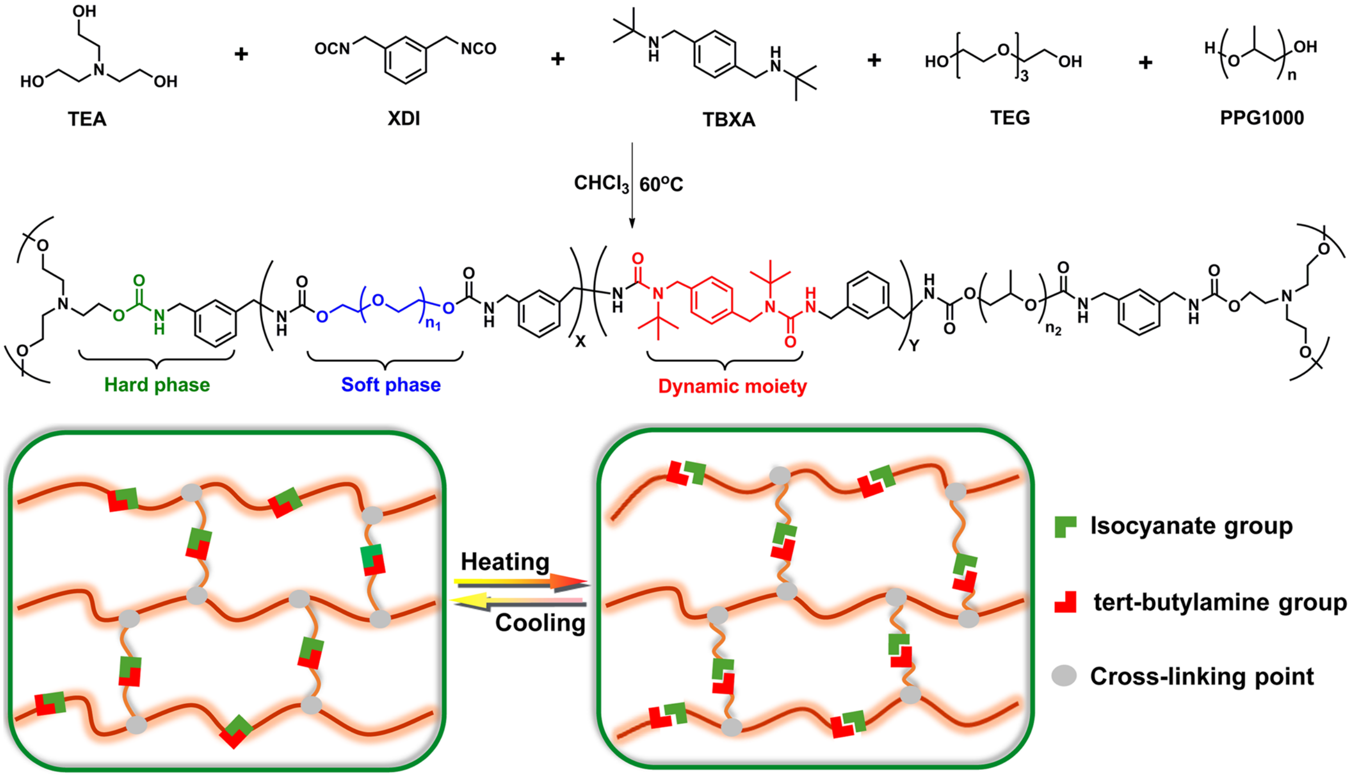


Figure 4. Schematic pathway for the synthesis of TBXA-based PUU networks.

The thermodynamic equilibrium constant K_{eq} of **2c** was studied through intermediate trapping experiments and determined to be 3.0×10^6 M^{-1} at 37 °C, independent of the concentration. In principle, when K_{eq} ranges from 10^{-7} to 10^7, the reaction is generally considered to be reversible.[28] k_{-1} was determined by monitoring the dynamic exchange kinetics of **2c** with butyl isocyanate, which was calculated to be 0.077 h^{-1}. The results indicated that the new HUB has a sufficiently large K_{eq} (~10^5) and k_{-1} to form polymers with a high molecular weight. It is worth noting that the k_{-1} value is lower than that of the TBEA-based system (1.2 h^{-1}), but the K_{eq} value is higher (7.9×10^5 M^{-1} for the TBEA-based system),[23] indicating a more stable structure.

Considering the fact that model dimer compounds are more similar to the actual structure of their polymer matrix, we further studied the K_{eq} and k_{-1} of the BisHUB model compounds. Although the bulky substituents in the HUBs make the urea bonds unstable, the HUBs still have a large K_{eq}. BisHUB model compound **3c** was studied in the same way as its monomeric analog **2c**. The K_{eq} and k_{-1} of bisHUB were 5.8 $\times 10^{12}$ M^{-2} (37 °C) and 0.12 h^{-1} (Figure 2b and Figure S15), respectively. The results demonstrated the presence of dynamic HUB exchange reactions in small molecules.

To demonstrate the metathesis property of HUBs based on this new diamine TBXA, two bisHUBs, **3c** and **6c**, were synthesized by mixing the corresponding isocyanate and TBXA in a 2:1 molar ratio. The mixing of the two parental bisHUBs resulted in the formation of a new HUB species (**7c**, Scheme S12), illustrated by the decreased intensity of a_1 (4.34 ppm) and a_3 (4.48 ppm) peaks and the growth of the a_4 (4.46 ppm) and a_6 (4.36 ppm) peaks (Figure 3a). Although the bond exchange conditions in bulky polymers are different from those of small molecules in solution, the model study confirmed the feasibility of using HUB exchange reactions as a temperature-dependent approach to obtaining a polymer network that is reversible.

Table 1. Thermal and Mechanical Characteristics of PUUs with Different Stoichiometric Ratios

samples	T_g[a] (°C)	$T_{5\%}$[b] (°C)	$T_{10\%}$[c] (°C)	$T_{d,max}$[d] (°C)	$R_{600°C}$[e] (%)	Young's modulus (MPa)	breaking stress (MPa)	elongation at break (%)
PUU-a	50.3	225	236	237, 354	14.2	132.7 ± 0.5	9.04 ± 1.4	292.8 ± 8
PUU-b	32.6	227	246	233, 353	12.5	7.77 ± 0.8	4.43 ± 1.8	402.5 ± 16
PUU-c	22.4	232	254	243, 352	10.9	1.52 ± 0.6	2.31 ± 1.7	529.5 ± 8.5
PUU-d	8.5	234	253	243, 352	10.3	0.28 ± 0.8	0.86 ± 1.8	1101 ± 12
PUU-e		281	316	363	21.2			
PUU-f	0.36	200	212	220, 325	1.30	0.51 ± 0.7	0.8 ± 1.2	641.7 ± 9.4

[a] T_g were obtained from the DMA results. [b] Thermal decomposition temperature at 5% weight loss. [c] Thermal decomposition temperature at 10% weight loss. [d] The maximum rate of the weight loss. [e] Residue weight at 600 °C.

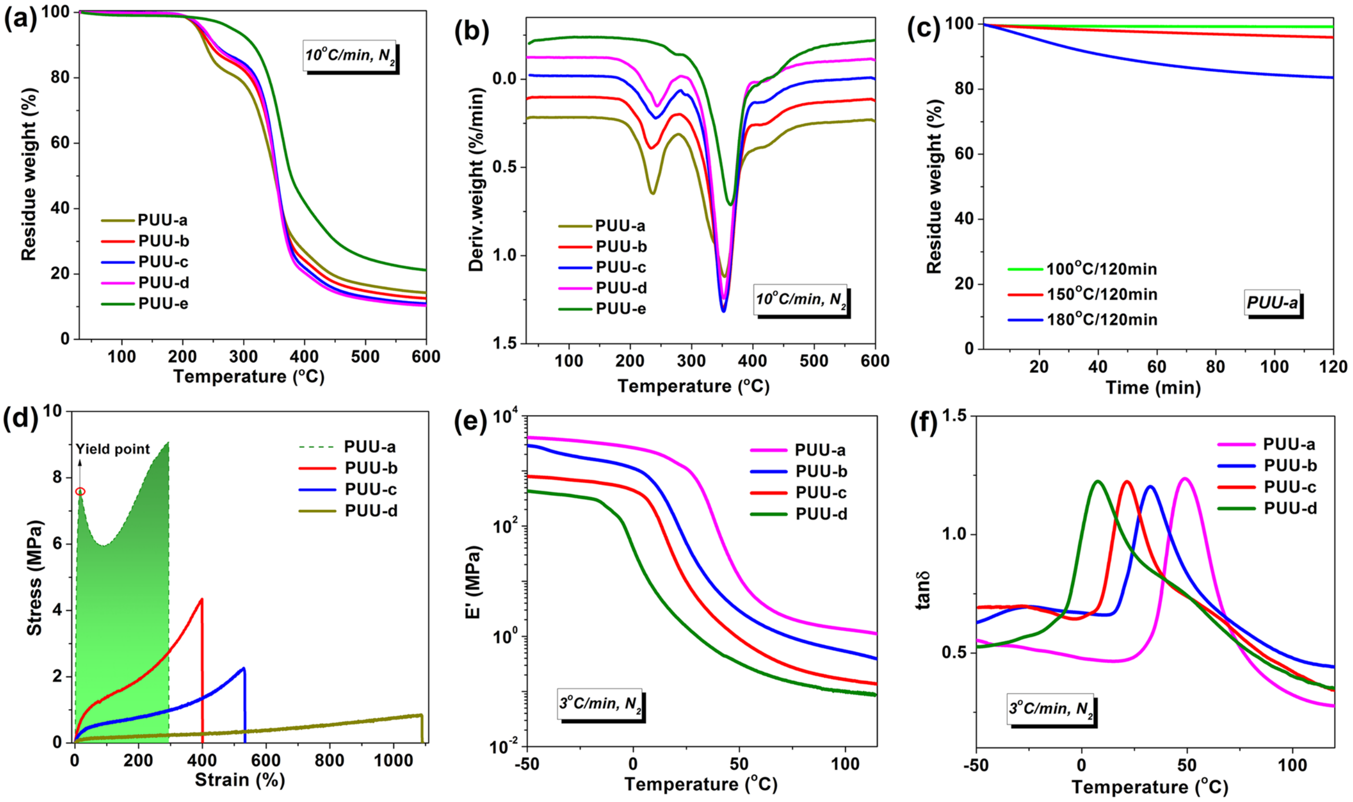


Figure 5. Thermal and mechanical properties of PUUs with different stoichiometric ratios. (a, b) TGA and DTG curves of PUUs under a nitrogen atmosphere. (c) Isothermal TGA curves of PUU-a under a nitrogen atmosphere. (d) Typical stress−strain curves of PUUs with a stretching speed of 20 mm/min. (e, f) E' and tan δ of PUUs obtained from DMA curves under a nitrogen atmosphere with a frequency of 1 Hz.

To further confirm the dynamic behavior of HUB in polymers, poly(**3a**/**3b**) was synthesized by mixing **3a** and **3b** in a 1:1 molar ratio and the M_n was 1.11 × 10^4 g/mol, as determined by GPC (Figure 3b, green curve, Scheme S13). The addition of another equivalent of **3b** led to the degradation of the polymer, and the low-molecular-weight (2.3 × 10^3 g/mol) molecules were obtained after incubation at 37 °C for 36 h (Figure 3b, blue curve). When 1 equiv of **3a** was readded to the solution, which restored the ratio of **3a**/**3b** to 1:1, the resulting polymer after 4 h incubation of the mixture at 37 °C showed a higher M_n (1.08 × 10^4 g/mol, Figure 3b, red curve), which overlaid perfectly with the original poly(**3a**/**3b**) GPC curve. The results demonstrate that HUBs based on the new diamine TBXA exhibit rapid exchange reactions in both HUB-based small molecules and polymers.

Synthesis and Characterization of HUB-Based PUUs. After demonstrating the dynamic exchange features of the new HUBs, we designed and synthesized several different kinds of catalyst-free PUU networks (Figure 4 and Table S1 and Table S2) from commercially available monomers. The successful polymerization of PUUs was explicitly demonstrated by the disappearance of the −NCO peak at 2264 cm^{-1} (Figure S16). The peaks at 1650 and 1718 cm^{-1} corresponded to the stretching vibrations of carbonyl C═O groups in urea and urethane,[29] respectively. Additionally, no residual curing exothermic peak was observed in the DSC thermograms, further confirming the complete curing of the PUU networks (Figure S17). Swelling experiments demonstrated good solvent resistance of the fully cured PUUs (Figure S18), which only swelled and were insoluble in organic solvents (Figure S19), even after heat treatment at 60 °C for 6 h (Figure S20).

Thermal and Mechanical Properties of HUB-Based PUUs. Thermal stability is a valuable parameter in practical applications of PUUs. DSC, DMA, and TGA measurements were employed to evaluate the thermal stability of HUB-based PUUs, and the corresponding data are summarized in Table 1. The PUU-e without dynamic HUB motifs and TBEA-based PUU-f were also studied as control. As expected, the aromatic-containing TBXA-based PUUs exhibited improved thermal stability compared to PUU-f due to the introduction of the rigid aromatic rings. DSC and DMA results indicated that the TBXA-based PUUs with different stoichiometric ratios showed higher T_g than the TBEA-based PUU-f (Table 1 and Figures S21 and S22). Due to the presence of soft and hard segments in the PUU networks, a higher soft segment fraction gave the PUUs sufficient chain mobility; thus, the T_g of PUUs decreased with increasing PPG content. For example, the T_g of PUU-a and PUU-d were 50.3 and 8.5 °C, respectively.

TGA results indicated that all the TBXA-based PUUs exhibit relatively good thermal stability, with the $T_{5\%}$ higher than 220 °C (Table 1), even higher than the poly(oximeurethane)s based on dynamic oxime−carbamate bonds.[30] The char yield of TBXA-based PUUs at 600 °C was all higher than 10% (Figure 5a), while that of TBEA-based PUU-f was only 1.3% (Figure S23). As reported by Rekondo and co-workers,[31] the char yield of poly(urea-urethane)s based on dynamic amine/urea exchange is 0 at about 405 °C. These results further demonstrated the better thermal stability of TBXA-based PUUs and were consistent with those of model compounds. As the PPG content increased, there was no significant difference in the $T_{5\%}$ of PUUs, but the char yield gradually decreased. The results suggested that a higher soft segment content led to a lower T_g and char yield of PUUs. It is worth noting that TBXA-based PUUs with different stoichiometric ratios revealed a two-step degradation process (Figure 5b), and an obvious weight loss peak at 225 °C was observed. This was associated with the evaporation of TBXA as the dynamic HUBs can reversibly dissociate into isocyanates and amines during heating. At the same time, it can be clearly seen from the DTG curve of TBXA that its $T_{d,max}$ was exactly 223 °C (Figure S5). TGA results of the PUU-e without dynamic HUB motifs provided additional evidence to support this conclusion as no weight loss peak at 225 °C was observed from the DTG curve of PUU-e. Meanwhile, the $T_{5\%}$ and char yield of PUU-e were higher than those of the TBXA-based PUUs.

Considering the fact that PUU materials are expected to experience high temperatures over long periods when being processed, the isothermal TGA curves of PUU-a and PUU-f at 100, 150, and 180 °C for 2 h were obtained. The results indicated that PUU-a was more stable than PUU-f when isothermally heated. For example, PUU-a showed a 4.0% weight loss after incubation at 150 °C for 2 h (Figure 5c and Figure S24), while PUU-f showed a 10% weight loss (Table S4). In addition, the FTIR spectrum of PUU-a after heat treatment at 150 °C for 5 h was nearly identical to that of the original one (Figure S25).

Tensile tests were conducted to characterize the mechanical properties of PUUs using a uniaxial tensile testing machine. Herein, the Young's modulus, breaking stress, and elongation at break obtained from the stress−strain curves are used to evaluate the mechanical properties. According to the UNE-EN-ISO 527 standard, a rectangular film sample with an effective gauge dimension of 30 mm $(L) \times 6$ mm $(W) \times 1$ mm (T) is needed to conduct the mechanical properties tests. Considering the fact that as-synthesized PUU samples are powder (such as PUU-a) or behave as a soft rubber at room temperature (such as PUU-d), they cannot meet the uniaxial tensile test requirements. Therefore, the cross-linked PUUs were first processed into rectangular films by means of compression molding under a certain pressure (3 MPa), temperature (80 °C), and time (60 min) before mechanical tests. Due to the dynamic nature of the HUB motifs, the TBXA-based PUUs showed excellent processability. Theoretically, this processing can be repeated as many times as desired, although this may cause aging of the material. All TBXA-based PUU samples showed excellent transparency properties with the optical transmittance of above 75% (Figure S26). In addition to good thermal properties, the aromatic-containing TBXA-based PUUs exhibited remarkably higher Young's moduli and breaking stresses than the PUU-f and the reported PUUs.[32,33] For example, the Young's modulus and breaking stress for PUU-a were 132.7 and 9.04 MPa (Figure 5d), respectively, while those for PUU-f were 0.51 and 0.8 MPa (Figure S27), respectively. In contrast, the cross-linked PUU-e without the HUB moiety is very difficult to hot-press. The appearance of PUU-e is uneven, the wrinkles can be clearly observed, and the edges are even sticking up (Figure S28). As a result, the mechanical property of PUU-e was extremely poor due to the poor malleability (Figure S29).

Especially, the aromatic-containing TBXA-based PUUs showed good mechanical property without sacrificing their stretchability. As shown in Figure 5d, the stress−strain curve of PUU-a can be divided into three distinct regions, similar to a rubber-like elastomer. In the first region, a steep increase in stress at a low strain was observed, reflecting the typical elastic deformation originating from covalent networks. Then, a yield point was observed at a strain of 16%, and a strain-softening region was observed in the second region, representing the occurrence of the disassociation of reversible HUBs and the partial motion of polymer chains. After that, the strain was increased to 90%, the strain hardening resulting from the orientation of polymer chains was observed along the stretching direction, and the maximum tensile strength was generated at a strain of 292.8%. As the PPG content increased, PUUs showed a lower Young's modulus and breaking stress, while the elongation at break was enhanced. PUU-d exhibited extreme stretchability with an elongation at break of 1101%. Therefore, the mechanical properties of TBXA-based PUUs can be easily tuned by adjusting the stoichiometry. In addition, increasing the stretching speed from 10 to 400 mm/min increased the Young's modulus and breaking stress for PUU-a, while the elongation at break decreased (Table S5). A maximum Young's modulus of 315.4 MPa was reached at a higher stretching speed (400 mm/min, Figure S30). As the stretching speed decreased, there was more time for the reconfiguration, reorientation, and displacement of polymer chains, which increased the fracture tolerance.[34]

Dynamic Viscoelastic Properties of PUUs. The dynamic viscoelastic properties of PUUs were explored by DMA in the tensile mode, and the network rearrangement was evaluated by stress relaxation experiments. All PUU samples showed similar temperature-dependent viscoelastic properties with high storage modulus (E') in the glassy state and low E' in the rubbery state. As the PPG content increased, the initial E' and T_g (determined from the peak value of the tan δ peak) of the PUUs decreased (Figure 5e), indicating an increase in the chain mobility of the molecular chains. For example, PUU-a displayed the highest T_g of 50.3 °C, while that for PUU-d was only 8.5 °C (Figure 5f). It is noteworthy that the E' of the PUUs continuously decreased as the temperature increased, especially around the glass transition, which was attributed to the transition from a glassy state to a highly elastic state.[35] The absence of the constant plateau modulus for HUB-based PUUs further indicated that the dynamic HUBs were based on the

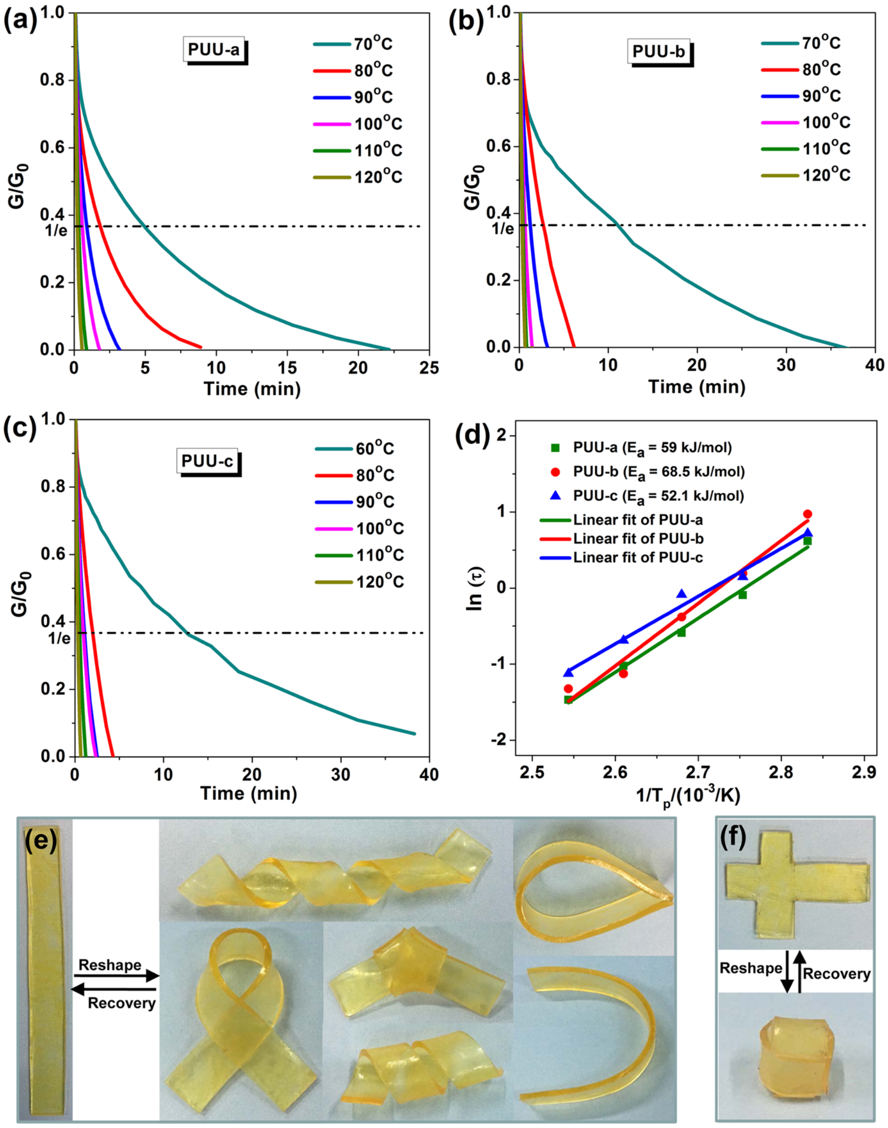


Figure 6. Dynamic viscoelastic properties and thermadapt behaviors of PUUs. (a–c) Normalized stress relaxation curves of PUU-a, PUU-b, and PUU-c. (d) Plots of the linear regression of the logarithm of relaxation time ln τ vs reciprocal of temperature $1/T$. (e, f) Visual demonstration of the shape memory process of PUU-c.

dissociative exchange mechanism, whereas such materials can experience fast topology rearrangements because of a decrease in network integrity.[36]

The time- and temperature-dependent stress relaxation behavior of the PUUs was also investigated by DMA. After achieving a specific temperature, a 1% strain was used, and the relaxation modulus was monitored as a function of time. By convention, the relaxation time (τ) was determined at 37% (1/e) of the normalized relaxation modulus, which was σ/σ_0 = 0.37.[37] As the temperature increased, the stress relaxation process of the PUU networks accelerated due to the rapid dissociation of dynamic HUBs, and ultimately, all PUUs underwent complete stress relaxation at high temperatures (Figure 6a–c, Figure S31). For example, the τ of PUU-a ranged from 5 min at 70 °C to 14 s at 120 °C. To our knowledge, no other cross-linked systems with a rigid polymer structure and the absence of a catalyst have shown such rapid stress relaxation. It is believed that the rapid stress relaxation of the PUUs was attributed to the rapid exchange reactions of dynamic HUBs and the resulting network rearrangement.

The temperature dependence of the relaxation time can be described by the Arrhenius equation, and an activation energy (E_a) can be calculated from the slope. Thus, the E_a for the stress relaxation is characteristic of the bond exchange process in the polymer networks.[38] For example, the E_a of the dynamic PUU-a was 59 kJ/mol (Figure 6d), which is lower than other reported PUU systems.[31,39,40] These results provide further evidence that a fast bond exchange reaction was embedded in a rigid polymer matrix even without the need of a catalyst,[41] leading to a lowering of the reaction barrier for exchange reactions. Such an exchange reaction is beneficial to the malleability, recyclability, and self-healing of the HUB-based PUUs.

Although HUB-based PUUs behave like a normal thermoset, they display thermoresponsive shape memory behavior. When the temperature is above the T_g, the mobility of PUU-c segments is enhanced. The conformation of molecular segments can be changed with external force, and the original shape is changed with the decrease in conformational entropy. When the deformed network is quickly cooled to a

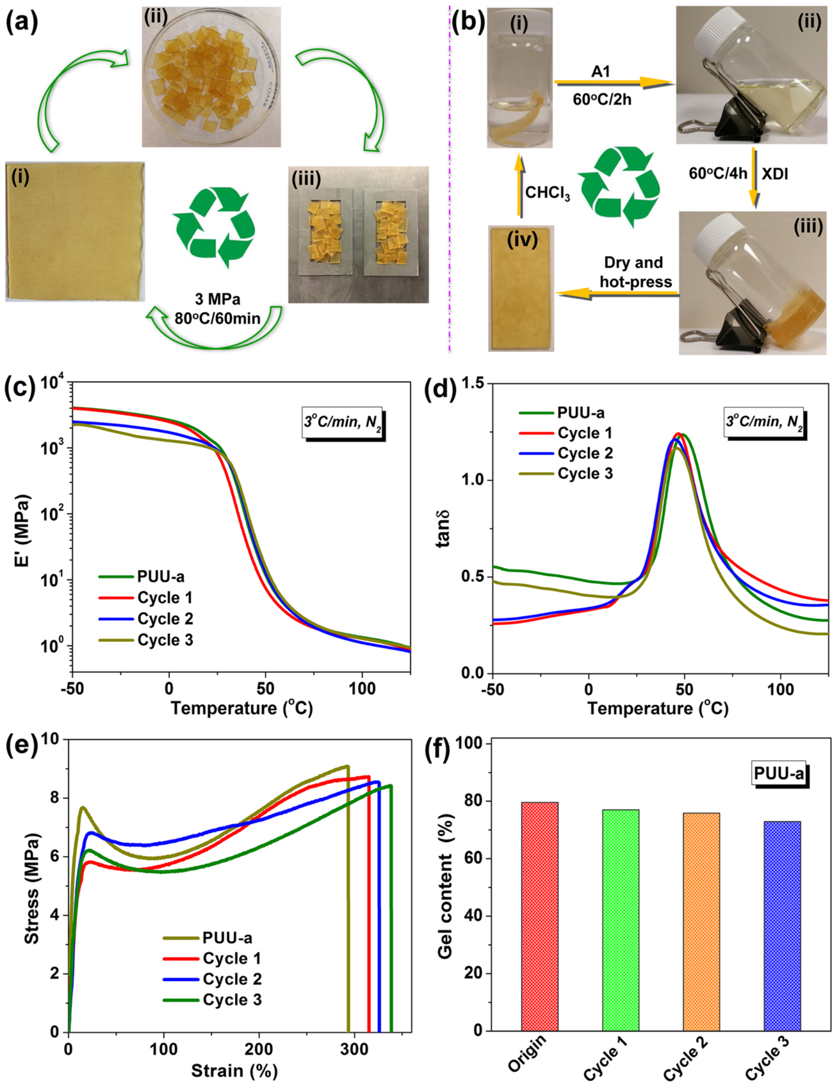


Figure 7. Recycling of PUU-a. (a) Photographs of PUU-a bulk material and after being reprocessed by compression molding for three repeated cycles (3 MPa, 80 °C, 60 min). (b) Degradation of PUU-a by excess TBXA and the reformed PUU-a by addition of XDI. (c, d) E' and tan δ curves of virgin and multiple recycled PUU-a samples. (e) Stress−strain curves of PUU-a through three generations of recycling. (f) Gel contents of virgin and multiple recycled PUU-a samples in $CHCl_3$.

temperature below the T_g, the mobility of molecular segments is greatly restrained, resulting in the fixation of the temporary shape under external force. As shown in Figure 6e, the PUU-c strip can bear knotting, bending, or twisting as the temporary shape without damage. In another example, a cross-shaped PUU-c can transiently fold to a cubic shape (Figure 6f). When the temperature increased again above the T_g, the mobility of molecular segments was regained and the temporary shape can revert back to the original shape.[42] The shape fixation and recovery processes can be attributed to the elasticity properties of the shape memory effect.[43]

Reprocessability and Recyclability of PUUs. The reprocessability and recyclability of the dynamic PUUs were explored via hot-pressing experiments using PUU-a, which displayed the best mechanical properties. This is a very demanding test as the transition from particle to coherent film requires perfect healing across thousands of interfaces between particles.[44] The solid phase recycling method of PUU-a was as follows: The PUU-a bulk film was cut into small pieces and then hot-pressed under a pressure of 3 MPa at 80 °C for 60 min to form a bulk material. A transparent and homogeneous PUU film was obtained, indicating the excellent reprocessability of PUUs (Figure 7a). The recycling process was repeated three times to ensure the reversibility, and then the recycled PUU samples were subjected to FTIR, DMA, and tensile and solubility tests. The results indicated that the PUU-a can be reprocessed and recycled under mild conditions while still maintaining their chemical and mechanical properties due to the dynamic reversibility of HUBs. The FTIR spectra of the recycled PUUs were nearly identical to that of the original one, and no obvious chemical degradation was observed (Figure S32). DMA results showed only a small decrease in T_g after multiple recycling of PUUs (Figure 7c,d), indicating a slightly decrease in the cross-linking density.

The stress−strain curves of the recycled PUU-a were consistent with those of the pristine one (Figure 7e). The recycled PUU-a exhibited no obvious decrease in their mechanical strength, and only a slight decrease in the breaking stress was observed (Table S6). Swelling experiments demonstrated that the multiple recycled PUU-a samples were insoluble in $CHCl_3$. The gel contents of the recycled PUU-a shown in Figure 7f demonstrated that the chemically cross-

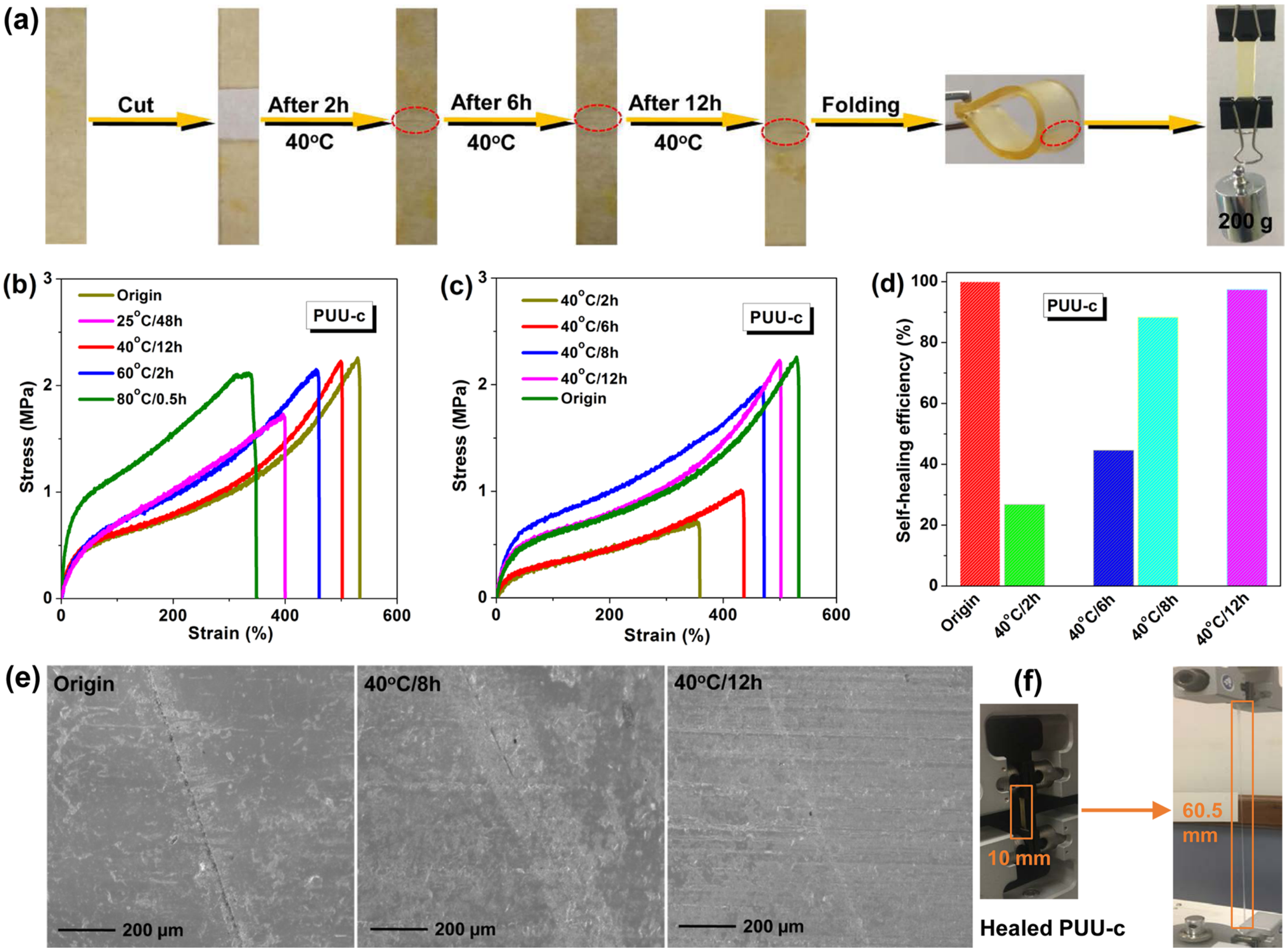


Figure 8. Self-healing properties of PUU-c. (a) Photographs of self-healing process of PUU-c. (b) Typical tensile stress−strain curves of original and healed PUU-c with different healing temperatures. (c, d) Stress−strain curves and self-healing efficiency of original and healed PUU-c with different healing times at 40 °C. (e) Optical microscopy images of the scratch on the PUU-c film. (f) Photographs of the healed PUU-c before and after stretching.

linked network of the recycled PUU-a was well maintained during the reprocessing cycles. Thus, due to the reversible nature of the HUB motifs, the catalyst-free PUUs exhibited excellent reprocessability and recyclability without chemical changes or loss of mechanical properties.

It is worth noting that the solid-phase recycling method was unable to restore the recovered products to raw materials, which greatly limits the practical applications. Herein, we verified that the dynamic PUU thermosets could be conveniently switched between oligomers and polymers by tuning the monomer ratio, which has been shown to significantly enhance the material's recycling efficiency.[45] As shown in Figure S19, when a rectangular film of PUU-a was immersed in $CHCl_3$ at room temperature, the specimen only showed swelling. However, the sample completely dissolved in $CHCl_3$ after adding 3 equiv of TBXA and incubating at 60 °C for 2 h (Figure 7b). It has been demonstrated that the dynamic HUBs that can reversibly generate isocyanates and amines at elevated temperatures play a key role in the dynamic properties of PUUs.[46] Thus, PUU-a chains were broken into soluble segments due to the dynamic exchange reactions of HUBs. Afterward, the PUU-a network was reformed by the addition of XDI with the same equivalence of functional groups as TBXA after incubating at 60 °C for 4 h. The reformed PUU-a was vacuum-dried and could be remolded into a square-shaped sample by hot-pressing. The results showed that the structure, T_g, and mechanical properties of the resolidified PUU-a were comparable to those before recycling (Figures S33 and S34 and Table S7). Therefore, this method provides unique advantages of broad processing windows and a flexible recycling strategy with attractive application potentials, such as the complete recovery of the resin matrix and expensive carbon fibers from resin-based composites.

Self-Healing Ability of PUUs. It is difficult for conventional PUUs with irreversible covalent bonds to self-heal after damage, and the cracked thermosets are generally repaired using glue. In contrast, dynamic polymeric materials provide a new paradigm for damage repair. Uniaxial tensile tests were conducted to quantify the mechanical recovery after treating under different conditions. The healing efficiency (%) is defined as the ratio of the stress of the healed and virgin materials. Generally, autonomous self-healing is accomplished in polymers with a low T_g because a lower T_g gives the polymer chains better mobility to facilitate chain diffusion, bond exchange, and re-entanglement at broken surfaces.[47] Actually, PUU-a with the highest T_g (50.3 °C) also possessed self-healing ability; however, a higher T_g restrained the mobility of polymer chains. It takes a long time for the PUU-a to complete self-healing, and only ∼41% of its original breaking stress recovered after incubation at 80 °C for 60 h (Figure S35). Thus, PUU-c with relatively lower T_g (22.4 °C) was chosen to examine the self-healing behavior of the TBXA-based PUUs.

Since polymer chains will restrain the mobility and decrease the reactivity of isocyanates and amines generated during the dissociation of HUBs, it takes time for the HUBs to complete reformation after heat treatment. The PUU-c film was cut into two separate pieces using a razor blade, and then the two pieces were brought into contact for 30 s (Figure 8a). The material was placed in an oven and treated at different temperatures without external force to initiate the healing process. The healing efficiency increased dramatically along with increasing healing temperature, which followed the general law of other self-healing materials.[30] For example, the scratches were healed within 30 min at 80 °C (Figure 8b and Table S8). In contrast, the high stability and irreversible nature of the three-dimensional cross-linked PUU-e without HUB moiety featured no scratch-healing ability.

To better understand the effect of the healing time on the healing efficiency, the temperature of 40 °C for a defined time was chosen. The TBXA-based PUU materials can also be self-healed at room temperature, but they also need a long time (25 °C, 48 h). After incubation at 40 °C for 12 h, the complete recovery of the mechanical properties for PUU-c was observed (Figure 8c and Table S9), and the healed sample could be folded and was able to sustain a weight of 200 g without rupture. The PUU-c reached a self-healing efficiency of up to 97.4% (Figure 8d). Optical microscopy was utilized to visually inspect the healing process. The scratch disappeared completely after healing treatment at 40 °C for 12 h (Figure 8e), and the healed sample can be stretched up to 505% of their original length without fracture (Figure 8f). The comparison of the mechanical performance and healing efficiency between TBXA-based PUUs and other materials is shown in Table S10. The results indicated that the highly-reversible HUBs endowed the TBXA-based PUU networks with efficient self-healing performance and acceptable mechanical properties after healing. The results also illustrated the necessity of heating thermosets above the T_g as the broken parts possessed better mobility, allowing the cracks to be healed through the diffusion and rearrangement of cracked fragments.

■ CONCLUSIONS

A new class of recyclable, self-healable, and highly malleable PUUs based on dynamic hindered urea bonds with improved thermal and mechanical performances were developed and systematically studied. Incorporation of the aromatic moiety-containing bulky diamine TBXA instead of TBEA can effectively block the degradation pathway of forming the five-member cyclic byproduct, thus enhancing the thermal and mechanical properties. The dynamic properties of TBXA-based HUBs were first confirmed in molecular model compounds and linear polymers. Then, TBXA was incorporated in a series of PUU networks, which demonstrated significantly improved thermal stability and mechanical strength compared to its TBEA-based counterparts. Apart from these, the dynamic viscoelastic and self-healing properties of these PUUs were systematically assessed. The rapid stress relaxation of the TBXA-based PUUs was obtained due to the rapid exchange reactions of dynamic HUBs, and the scratch can be effectively healed at a low temperature of 40 °C. More importantly, the PUUs could be reprocessed multiple times without compromising their chemical or mechanical properties. We envision that this work will provide an easy and scalable approach for the preparation of PUUs with a combination of excellent reprocessability, recyclability, and self-healing ability.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c07553.

Determination of K_{eq} and k_{-1} of monoHUB and bisHUB, dynamic exchanges of HUB-bearing polymers, characterization details, structural formula of the model compounds, ^{1}HNMR spectra, FTIR, DSC, TGA, DMA, stress−strain curves, and stress-relaxation curves (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Shujuan Wang − *Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States; School of Chemistry, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China*; Email: shujuanwang@mail.xjtu.edu.cn

Jianjun Cheng − *Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States*; orcid.org/0000-0003-2561-9291; Email: jianjunc@illinois.edu

Authors

Yingfeng Yang − *Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States*

Hanze Ying − *Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States*

Xinli Jing − *School of Chemistry and MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China; Xi'an Key Laboratory of Sustainable Energy Material Chemistry, Xi'an, Shaanxi 710049, China*

Bin Wang − *School of Chemistry, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China*

Yanfeng Zhang − *School of Chemistry, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China*; orcid.org/0000-0003-4711-8690

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.0c07553

Author Contributions

⊥S.W and Y.Y. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China (nos. 51703179, 11732012), National Key Research and Development Program of China (no. 2019YFA0706801), Fundamental Research Funds for the Central Universities (no. xjh012019024), China Scholarship Council awarded to S.W, and United States National Science

Foundation funding (CHE 1508710) awarded to J.C. We also acknowledge the Instrument Analysis Centre of Xi'an Jiaotong University for material characterization.

REFERENCES

(1) Long, T. E. Toward Recyclable Thermosets. *Science* **2014**, *344*, 706−707.
(2) Albertsson, A. C.; Hakkarainen, M. Designed to Degrade. *Science* **2017**, *358*, 872−873.
(3) Zhu, J.-B.; Watson, E. M.; Tang, J.; Chen, E. Y.-X. A Synthetic Polymer System with Repeatable Chemical Recydability. *Science* **2018**, *360*, 398−403.
(4) Jiang, L.; Liu, Z.; Lei, Y.; Yuan, Y.; Wu, B.; Lei, J. Sustainable Thermosetting Polyurea Vitrimers Based on a Catalyst-Free Process with Reprocessability, Permanent Shape Reconfiguration and Self-Healing Performance. *ACS Appl. Polym. Mater.* **2019**, *1*, 3261−3268.
(5) Scheutz, G. M.; Lessard, J. J.; Sims, M. B.; Sumerlin, B. S. Adaptable Crosslinks in Polymeric Materials: Resolving the Intersection of Thermoplastics and Thermosets. *J. Am. Chem. Soc.* **2019**, *141*, 16181−16196.
(6) Zhao, B.; Ding, H.; Xu, S.; Zheng, S. Organic-Inorganic Linear Segmented Polyurethanes Simultaneously Having Shape Recovery and Self-Healing Properties. *ACS Appl. Polym. Mater.* **2019**, *1*, 3174−3184.
(7) Jehanno, C.; Sardon, H. Dynamic polymer network points the way to truly recyclable plastics. *Nature* **2019**, *568*, 467−468.
(8) Zou, W.; Dong, J.; Luo, Y.; Zhao, Q.; Xie, T. Dynamic Covalent Polymer Networks: From Old Chemistry to Modern Day Innovations. *Adv. Mater.* **2017**, *29*, 1606100.
(9) Kloxin, C. J.; Bowman, C. N. Covalent Adaptable Networks: Smart, Reconfigurable and Responsive Network Systems. *Chem. Soc. Rev.* **2013**, *42*, 7161−7173.
(10) Bowman, C. N.; Kloxin, C. J. Covalent Adaptable Networks: Reversible Bond Structures Incorporated in Polymer Networks. *Angew. Chem., Int. Ed.* **2012**, *51*, 4272−4274.
(11) Wang, S.; Xing, X.; Zhang, X.; Wang, X.; Jing, X. Room-Temperature Fully Recyclable Carbon Fibre Reinforced Phenolic Composites Through Dynamic Covalent Boronic Ester Bonds. *J. Mater. Chem. A* **2018**, *6*, 10868−10878.
(12) Zhang, Z. P.; Rong, M. Z.; Zhang, M. Q. Polymer Engineering Based on Reversible Covalent Chemistry: A Promising Innovative Pathway Towards New Materials and New Functionalities. *Prog. Polym. Sci.* **2018**, *80*, 39−93.
(13) Taynton, P.; Yu, K.; Shoemaker, R. K.; Jin, Y.; Qi, H. J.; Zhang, W. Heat- or Water-Driven Malleability in a Highly Recyclable Covalent Network Polymer. *Adv. Mater.* **2014**, *26*, 3938−3942.
(14) Christensen, P. R.; Scheuermann, A. M.; Loeffler, K. E.; Helms, B. A. Closed-Loop Recycling of Plastics Enabled by Dynamic Covalent Diketoenamine Bonds. *Nat. Chem.* **2019**, *11*, 442−448.
(15) Truong, T. T.; Thai, S. H.; Nguyen, H. T.; Phung, D. T. T.; Nguyen, L. T.; Pham, H. Q.; Nguyen, L. T. T. Tailoring the Hard-Soft Interface with Dynamic Diels-Alder Linkages in Polyurethanes: Toward Superior Mechanical Properties and Healability at Mild Temperature. *Chem. Mater.* **2019**, *31*, 2347−2357.
(16) Ma, S.; Webster, D. C. Degradable Thermosets Based on Labile Bonds or Linkages: A Review. *Prog. Polym. Sci.* **2018**, *76*, 65−110.
(17) Li, J.; Nowak, P.; Otto, S. Dynamic Combinatorial Libraries: From Exploring Molecular Recognition to Systems Chemistry. *J. Am. Chem. Soc.* **2013**, *135*, 9222−9239.
(18) Zheng, N.; Hou, J.; Xu, Y.; Fang, Z.; Zou, W.; Zhao, Q.; Xie, T. Catalyst-Free Thermoset Polyurethane with Permanent Shape Reconfigurability and Highly Tunable Triple-Shape Memory Performance. *ACS Macro Lett.* **2017**, *6*, 326−330.
(19) Jin, Y.; Yu, C.; Denman, R. J.; Zhang, W. Recent Advances in Dynamic Covalent Chemistry. *Chem. Soc. Rev.* **2013**, *42*, 6634−6654.
(20) Cai, K.; Ying, H.; Cheng, J. Dynamic Ureas With Fast and pH-Independent Hydrolytic Kinetics. *Chem. − Eur. J.* **2018**, *24*, 7345−7348.
(21) Ying, H.; Cheng, J. Hydrolyzable Polyureas Bearing Hindered Urea Bonds. *J. Am. Chem. Soc.* **2014**, *136*, 16974−16977.
(22) Zhang, Y.; Ying, H.; Hart, K. R.; Wu, Y.; Hsu, A. J.; Coppola, A. M.; Kim, T. A.; Yang, K.; Sottos, N. R.; White, S. R.; Cheng, J. Malleable and Recyclable Poly(urea-urethane) Thermosets Bearing Hindered Urea Bonds. *Adv. Mater.* **2016**, *28*, 7646−7651.
(23) Ying, H.; Zhang, Y.; Cheng, J. Dynamic Urea Bond for the Design of Reversible and Self-Healing Polymers. *Nat. Commun.* **2014**, *5*, 3218−3227.
(24) Jia, Y.; Ying, H.; Zhang, Y.; He, H.; Cheng, J. Reconfigurable Poly(urea-urethane) Thermoset Based on Hindered Urea Bonds with Triple-Shape-Memory Performance. *Macromol. Chem. Phys.* **2019**, *220*, 1900148−1900155.
(25) Nevejans, S.; Ballard, N.; Fernández, M.; Reck, B.; García, S. J.; Asua, J. M. The Challenges of Obtaining Mechanical Strength in Self-Healing Polymers Containing Dynamic Covalent Bonds. *Polymer* **2019**, *179*, 121670.
(26) Xia, Q.; Chen, L.; Zhu, Y.; Shao, Z.; Guo, M. Stretchy and Strong Polyurethane−Urea Supramolecular (PUUS) Hydrogels with Various Stimulus-Responsive Behaviours: The Effect of Chain-Extenders. *J. Mater. Chem. B* **2019**, *7*, 1734−1740.
(27) Lei, Z.; Jia, J.; Wu, Q.; Zhang, J.; Wang, Y.; Jing, X.; Liu, Y. Curing Behavior and Microstructure of Epoxy-POSS Modified Novolac Phenolic Resin with Different Substitution Degree. *Polymer* **2019**, *178*, 121587−121601.
(28) Zhao, D.; Moore, J. S. Nucleation-Elongation: A Mechanism for Cooperative Supramolecular Polymerization. *Org. Biomol. Chem.* **2003**, *1*, 3471−3491.
(29) Fan, W.; Jin, Y.; Shi, L.; Zhou, R.; Du, W. Developing Visible-Light-Induced Dynamic Aromatic Schiff Base Bonds for Room-Temperature Self-Healable and Reprocessable Waterborne Polyurethanes with High Mechanical Properties. *J. Mater. Chem. A* **2020**, *8*, 6757−6767.
(30) Fu, D.; Pu, W.; Wang, Z.; Lu, X.; Sun, S.; Yu, C.; Xia, H. A Facile Dynamic Crosslinked Healable Poly(oximeurethane) Elastomer with High Elastic Recovery and Recyclability. *J. Mater. Chem. A* **2018**, *6*, 18154−18164.
(31) Erice, A.; de Luzuriaga, A. R.; Matxain, J. M.; Ruipérez, F.; Asua, J. M.; Grande, H.-J.; Rekondo, A. Reprocessable and Recyclable Crosslinked Poly(urea-urethane)s Based on Dynamic Amine/Urea Exchange. *Polymer* **2018**, *145*, 127−136.
(32) Fang, Z.; Zheng, N.; Zhao, Q.; Xie, T. Healable, Reconfigurable, Reprocessable Thermoset Shape Memory Polymer with Highly Tunable Topological Rearrangement Kinetics. *ACS Appl. Mater. Interfaces* **2017**, *9*, 22077−22082.
(33) Fang, Z.; Song, H.; Zhang, Y.; Jin, B.; Wu, J.; Zhao, Q.; Xie, T. Modular 4D Printing via Interfacial Welding of Digital Light-Controllable Dynamic Covalent Polymer Networks. *Matter* **2020**, *2*, 1187−1197.
(34) Miwa, Y.; Kurachi, J.; Kohbara, Y.; Kutsumizu, S. Dynamic Ionic Crosslinks Enable High Strength and Ultrastretchability in a Single Elastomer. *Commun. Chem.* **2018**, *1*, 5−8.
(35) Rehman, H. U.; Chen, Y.; Hedenqvist, M. S.; Li, H.; Xue, W.; Guo, Y.; Guo, Y.; Duan, H.; Liu, H. Self-Healing Shape Memory PUPCL Copolymer with High Cycle Life. *Adv. Funct. Mater.* **2018**, *28*, 1704109−1704122.
(36) Tang, Z.; Liu, Y.; Guo, B.; Zhang, L. Malleable, Mechanically Strong, and Adaptive Elastomers Enabled by Interfacial Exchangeable Bonds. *Macromolecules* **2017**, *50*, 7584−7592.
(37) Denissen, W.; Rivero, G.; Nicolaÿ, R.; Leibler, L.; Winne, J. M.; Du Prez, F. E. Vinylogous Urethane Vitrimers. *Adv. Funct. Mater.* **2015**, *25*, 2451−2457.
(38) Chao, A.; Zhang, D. Investigation of Secondary Amine-Derived Aminal Bond Exchange Toward the Development of Covalent Adaptable Networks. *Macromolecules* **2019**, *52*, 495−503.
(39) Zhang, L.; Rowan, S. J. Effect of Sterics and Degree of Cross-Linking on the Mechanical Properties of Dynamic Poly(alkylurea-urethane) Networks. *Macromolecules* **2017**, *50*, 5051−5060.

(40) Zhang, Z. P.; Rong, M. Z.; Zhang, M. Q. Mechanically Robust, Self-Healable, and Highly Stretchable 'Living' Crosslinked Polyurethane Based on a Reversible C-C Bond. *Adv. Funct. Mater.* **2018**, *28*, 1706050−1706058.

(41) de Luzuriaga, A. R.; Martin, R.; Markaide, N.; Rekondo, A.; Cabañero, G.; Rodríguez, J.; Odriozola, I. Epoxy Resin with Exchangeable Disulfide Crosslinks to Obtain Reprocessable, Repairable and Recyclable Fiber-Reinforced Thermoset Composites. *Mater. Horiz.* **2016**, *3*, 241−247.

(42) Ding, Z.; Yuan, L.; Liang, G.; Gu, A. Thermally Resistant Thermadapt Shape Memory Crosslinked Polymers Based on Silyl Ether Dynamic Covalent Linkages for Self-Folding and Self-Deployable Smart 3D Structures. *J. Mater. Chem. A* **2019**, *7*, 9736−9747.

(43) Zheng, N.; Fang, Z.; Zou, W.; Zhao, Q.; Xie, T. Thermoset Shape-Memory Polyurethane with Intrinsic Plasticity Enabled by Transcarbamoylation. *Angew. Chem., Int. Ed.* **2016**, *55*, 11421−11425.

(44) Zhang, B.; Kowsari, K.; Serjouei, A.; Dunn, M. L.; Ge, Q. Reprocessable Thermosets for Sustainable Three-Dimensional Printing. *Nat. Commun.* **2018**, *9*, 1831−1838.

(45) Lei, H.; Wang, S.; Liaw, D. J.; Cheng, Y.; Yang, X.; Tan, J.; Chen, X.; Gu, J.; Zhang, Y. Tunable and Processable Shape-Memory Materials Based on Solvent-Free, Catalyst-Free Polycondensation between Formaldehyde and Diamine at Room Temperature. *ACS Macro Lett.* **2019**, *8*, 582−587.

(46) Simón, D.; Borreguero, A. M.; de Lucas, A.; Rodríguez, J. F. Recycling of Polyurethanes From Laboratory to Industry, a Journey Towards the Sustainability. *Waste Manage.* **2018**, *76*, 147−171.

(47) Tan, Y. J.; Wu, J.; Li, H.; Tee, B. C. K. Self-Healing Electronic Materials for a Smart and Sustainable Future. *ACS Appl. Mater. Interfaces* **2018**, *10*, 15331−15345.