Reconfigurable Poly(urea-urethane) Thermoset Based on Hindered Urea Bonds with Triple-Shape-Memory Performance

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Thermoset shape memory polymers (SMPs) have a series of advantages in practical applications when compared with thermoplastic SMPs. However, the reprocessing and reshaping of thermosets are difficult due to the covalent crosslinking which severely limits the reconfiguration of polymer networks even under high temperature. Here, hinered urea bond (HUB), a urea bearing a bulky substituent on its nitrogen atom that can reversibly dissociate to the corresponding bulky amine and isocyanate, is integrated into the poly(urea-urethane) (PUU) crosslinked networks, enabling the networks to topologically reconfigure to other structures. Instead of having to cure the thermoset in a mold, the incorporation of HUBs can decouple the synthesis and shape-forming steps, which is a huge advantage for the processing of thermoset materials compared to conventional thermosets. This new PUU thermoset shows a broad glass transition behavior and exhibits excellent triple-shape-memory performance. With the incorporation of this dynamic urea bonds, permanent shapes can be flexibly tuned via the network reconfiguration, which is often neglected but significant to the practical application of SMPs.

1. Introduction

Shape memory polymers (SMPs), which are of great significance in a broad range of applications including aerospace structures, flexible electronics, smart actuators, sensors, and biomedicine,[1] have attracted much attention during the past decades. Most SMPs are dual-shape memory polymers which can store one temporary shape when subjected to a thermo-mechanical programming including deforming at temperature higher than transition temperature (T_{trans}) followed by cooling

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down to room temperature. When heated up to T_{trans}, the temporary shapes will return to the permanent shapes. However, the ultimate potential for the SMPs is limited by the number of shapes it can memorize in each shape memory cycle for the desired applications.[2] Recently, based on advanced macromolecular compositions or polymer networks, multiple SMPs capable of memorizing three or more shapes were designed, which greatly extended the potentials of SMPs. Basically, multiple SMPs can be prepared by introducing polymer domains with several different T_{trans} and careful tuning of the weight composition of different domains in the SMP networks.[3] However, the preparation of a polymer/polymer blend with more than two distinctive T_{trans} and good compatibility is extremely challenging. The strategy of designing SMPs with broad T_{trans} ranges was developed to achieve multiple-SMPs with much simpler polymer structure design and synthesis.[4] For example, Nafion, a perfluorosulphonic acid ionomer with crosslinked structure can store multiple shapes when subjected to the thermo-mechanical programming steps, which stems from its broad T_{trans} range (about 55–130 °C).[2] This sort of multiple SMPs can store intermediate shapes by programming steps without changing polymer composition, representing a real advantage in terms of design and synthesis of multiple SMPs.[5]

Depending on the thermal processibility, SMPs can be divided into thermoplastic and thermoset. Thermoplastic SMPs are easy to process but are limited by their lower abrasion/solvent resistances and structural stability at high temperature.[6] In contrast, thermoset SMPs have better mechanical/thermal/environmental resistance and superior high-temperature structural stability.[7] However, unlike thermoplastics, the thermoset SMPs must be prepared in a mold having desired shape because the thermoset SMPs are not able to be reshaped or reprocessed by heat or solvent after the formation of crosslinked networks. Thanks to the reversible (breaking and reforming) nature of recently developed dynamic covalent bonds (DCBs), the crosslinked networks based on these new chemistries can be topologically reconfigurable under external force and suitable temperature; hence, the thermoset can be reshaped to other geometries. In addition, the incorporation of dynamic covalent bonds can also

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decouple the synthesis and shape-forming steps, which is a huge advantage over conventional thermoset SMPs, as many complex shapes can be fabricated in a mold-free manner solid-state plasticity. These DCB-based thermoset SMPs have a unique material behavior, thermal adaptability; thus, this type of SMP can be precisely described as thermadapt SMP.[8] Since Leibler and co-workers proposed the reversible and malleable thermoset based on transesterification,[7] a variety of dynamic chemistries, such as temperature-induced transalkylation exchanges of C—N bond,[9] imine chemistry,[10] dynamic boronic ester bonds,[11] reversible click chemistry,[12] para-formaldehyde condensation with diamines,[13] dioxaborolane metathesis,[6] disulfide metathesis,[14] transcarbamoylation,[15] reversible radical association–dissociation,[16] and retro Diels–Alder,[17] have been used to develop self-healing, shape memory, malleable thermoset, and environmentally adaptive materials.[18] However, most of these reported systems are limited by the lack of low-cost raw materials. Also, most of these topological rearrangements have slow kinetics with long stress relaxation times under high temperatures,[7,9,15a,17a,19] which reduces the efficiency of polymer reprocessing.

We recently discovered and demonstrated that hindered urea bonds (HUBs) are dynamic (**Figure 1**a) under mild/catalyst-free conditions.[18b,20] From materials design standpoint, it is very easy to integrate HUBs into any polyurethane systems via the reaction between isocyanates and amines, and the thermal transition property of the polyurethane can be easily tuned via selecting of commodity and diverse monomers (crosslinkers, isocyanates, and chain extenders), which enables practical applications. Given the low cost of raw materials for HUBs, facile synthesis processes, and 100% monomer (isocyanates and amines) conversion, it is very promising to incorporate HUBs as dynamic linkages in designs of reconfigurable polyurethane thermoset with multiple shape memory property. Here, we report a reconfigurable poly(urea-urethane) (PUU) thermoset with triple-shape-memory behaviors based on HUBs and well-established polyurethane chemistry. As shown in Figure 1b, 1,1,1-tris(hydroxymethyl)propane (TMP) was used as crosslinker. 1,3-Bis(isocyanatomethyl)cyclohexane (BIMCH) and N,N′-di-tert-butylethylenediamine (DTBEA) were used to synthesize dynamic urea linkages. Polycaprolactone diol (PCL diol, $M_W = 2000$) was used as chain extender to tune the flexibility of the network. Dibutyltin dilaurate (DBTDL) was used to catalyze the reaction between hydroxyl and isocyanate.

2. Results and Discussion

The progress of the reaction was monitored by the disappearance of isocyanate peak in the FTIR spectrum (about 2250 cm^{-1}, Figure S2, Supporting Information). It should be noted that the as-synthesized PUU networks contain hindered urea, urethane bonds, and ester groups (in PCL diol) and all those have been reported to be dynamic under certain conditions.[7,21] However, the reversible behavior of this PUU is mostly from HUBs as transcarbamoylation (exchange reaction of urethane bonds) is slow and often needs extremely high temperatures with undesirable side reactions.[15a] It

was reported that polyurethane thermoset (crosslinker/chain extender ratio = 3:1) needs as long as 125 min at 170 °C to relax the inner stress to zero.[21b] DBTDL can accelerate the stress relaxation and lower the relaxation temperature, but only for low crosslinking (crosslinker/chain extender ratio = 1:30) polyurethane systems,[15b] while the transesterification rate will be greatly influenced by the catalyst types and contents.[21c,22] To confirm the dominant role of HUBs in the reversible property, we also designed several contrast samples using polyethylene glycol (PEG) and different content of HUBs as shown in **Table 1** and ran the stress relaxation tests under the same temperature (Figure 1c). The relaxation of PU-PCL containing ester groups was indeed faster than PU-PEG: the relaxation time (τ^*, the time needed to relax the inner stress to 37%)[7] of PU-PCL was 57.0 min while the τ^* of PU-PEG was 66.1 min and both needed more than 400 min to fully relax. Interestingly, the τ^* showed a large decrease (7.8 min) when HUBs were introduced (PUU-1) and the τ^* value became even smaller with the increase of HUB content (PUU-2 and PUU-3). It should be noted that all the τ^* values became smaller when the temperature was increased to 150 °C. However, the relaxation of PUU-1 was still much faster than PU-PEG and PU-PCL (Figure S3, Supporting Information). In this study, we focused on PUU-1 with a gel content of 97.8% (gel content, Supporting Information). As shown in Figure 1d, the τ^* reduced as the increase of temperature and the activation energy was calculated to be 101.4 kJ mol^{-1} K^{-1} via Arrhenius analysis[9] (Figure 1e). When the temperature was 150 °C, τ^* was as low as 42 s and the inner stress only needed 4.2 min to fully relax. Other than the fast reconfigurability, the PUU-1 also showed good mechanical property with a tensile strength of 40.5 ± 1.3 MPa and a Young's modulus of 0.76 ± 0.06 GPa (Figure S4 and Table S1, Supporting Information). To macroscopically observe the stress relaxation behavior from the view point of materials, a piece of film was exposed to 150 °C environment for 10 min while keeping the external force (Figure 1f). After that the external force was removed and a free-standing 3D shape was successfully created. When it was reheated to 150 °C, this free-standing 3D shape did not recover. The reason is that under the external stimulus (temperature and force), the crosslinked networks reconfigured to the highest entropic state, which corresponded to the complete stress relaxation; thus, the deformation could not recover due to the lack of entropic driving force.[15b] It is worth noting that this reconfiguration contains both chemical and physical processes. The chemical process is the topological rearrangement via the exchange reaction between isocyanates and *tert*-butyl-amino groups which leads to the complete stress relaxation. Although stress relaxation is quite common for polymers, the stress relaxation of conventional thermoset cannot reach zero [15b]; therefore, the dynamic HUB chemistry is the decisive factor for the shape tunability of this PUU thermoset, while the physical process is the conformation transformation of molecular chains, indicating that the permanent shape of this crosslinked PUU can be tuned by chemical and physical evolution. As contrast, the shape tunability of thermoplastic materials is only ascribed to the breaking and reforming of physical intermolecular force.
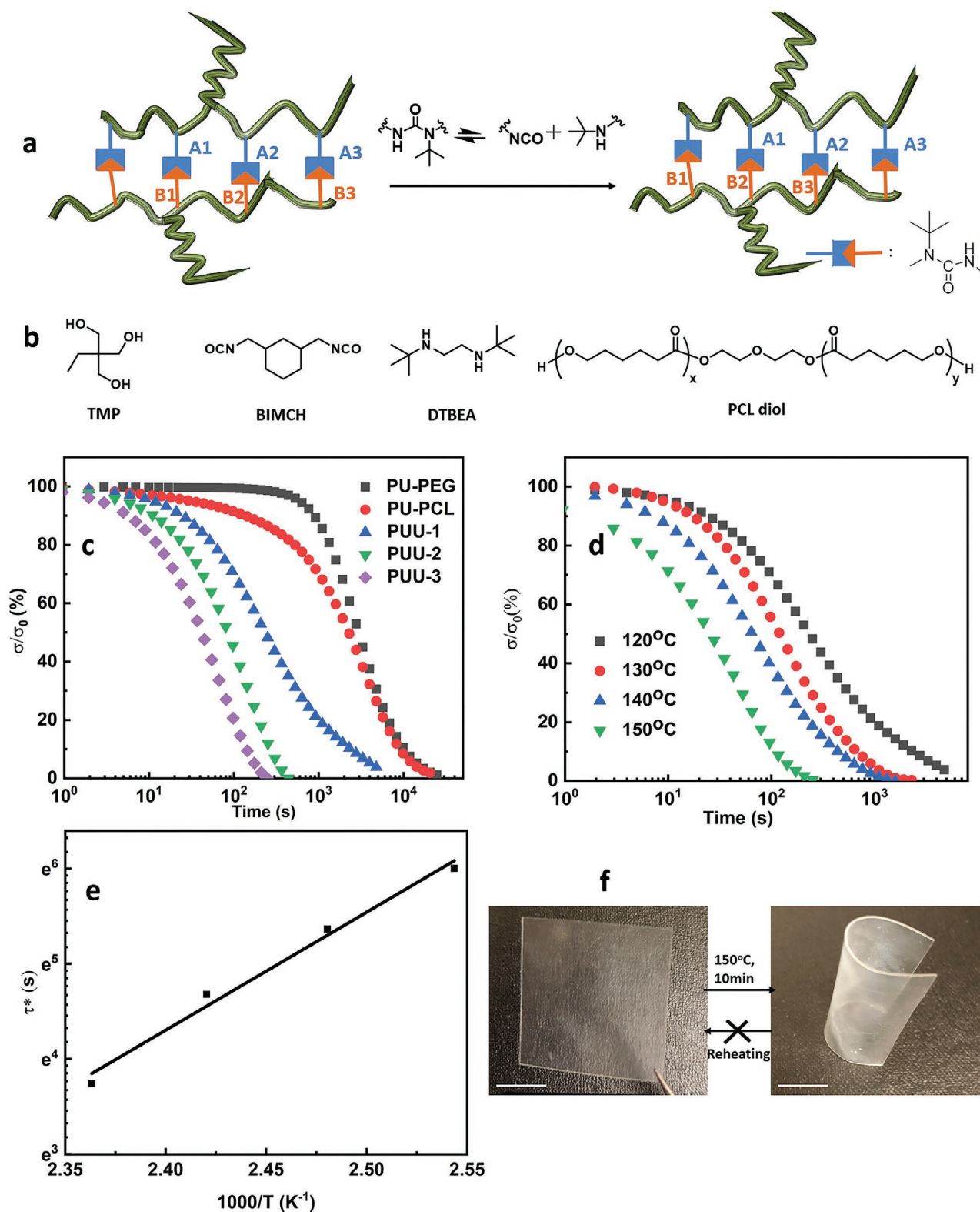
Figure 1. a) Schematic diagram of the reconfiguration of crosslinked networks via dynamic property of HUBs; b) chemical structures and formulations used for the synthesis of PUU; c) stress relaxation of contrast sample under 120 °C; d) stress relaxation of PUU-1 under different temperatures; e) Arrhenius analysis for PUU-1; f) PUU-1 thermoset can be reshaped to another free-standing shape (scale bar = 1 cm).

Table 1. Formulations of as-designed PUU and contrast samples.

Sample name	TMP (equiv.)	BIMCH (equiv.)	DTBEA (equiv.)	PCL diol (equiv.)	PEG (equiv.)
PU-PEG	4.7	8.0	/	/	1.0
PU-PCL	4.7	8.0	/	1.0	/
PUU-1	4.7	14.0	6.0	1.0	/
PUU-2	4.7	20.0	12.0	1.0	/
PUU-3	4.7	26.0	18.0	1.0	/

We then conducted the creep study of PUU-1 under constant force with temperature sweep from room temperature (RT) to 170 °C (**Figure 2**a). Other than the sharp increase of the strain over 140 °C due to the fast relaxation behavior of HUB, we also identified a phase transition range from 60 to 110 °C from the curve. We then performed dynamic mechanical analysis to further examine the thermal–mechanical behavior in this range. As shown in Figure 2b, tan δ peak around 60 to 110 °C indicated that PUU-1 showed a broad glass transition range.[23] Orders of magnitude modulus change over the T_g is a prerequisite for the materials to exhibit efficient shape memory behaviors,[24] and the broad transition range may hint the potential for multiple SMP.

First, we picked 85 °C as the T_{trans} to study the classical dual-shape memory behaviors. As shown in Figure 2c, the reshaped PUU thermoset from Figure 1f and a ribbon were deformed at 85 °C, respectively. The external force was maintained and the specimens were cooled down to room temperature. After that, the temporary shapes were well fixed and when the temporary shapes were brought up back to 85 °C, they transferred back to their permanent shapes. Excellent dual-shape memory efficiency (shape fixity ration = 99.2%, shape recovery ratio = 97.4%; the test methods can be found in Supporting Information) was shown in the quantitative test (Figure 2d). The shape memory behaviors in the cyclic thermomechanical programming also showed great cycle stability. Even when subjected to a large strain at T_{trans}, PUU-1 still showed great shape fixity and recovery ratios (Figure S1, Supporting Information).

We then tested if the broad glass transition range (60–110 °C) supplies PUU-1 with feasibility to exhibit triple-shape-memory behaviors. As shown in **Figure 3**a, PUU-1 specimen was first deformed at 100 °C and fixed at 60 °C for its first temporary shape. Next, the specimen was given the second temporary shape and fixed at room temperature. After that, the specimen was heated up and kept at 60 °C. We were able to observe the transition from the second temporary shape to the first temporary shape. Similarly, when PUU-1
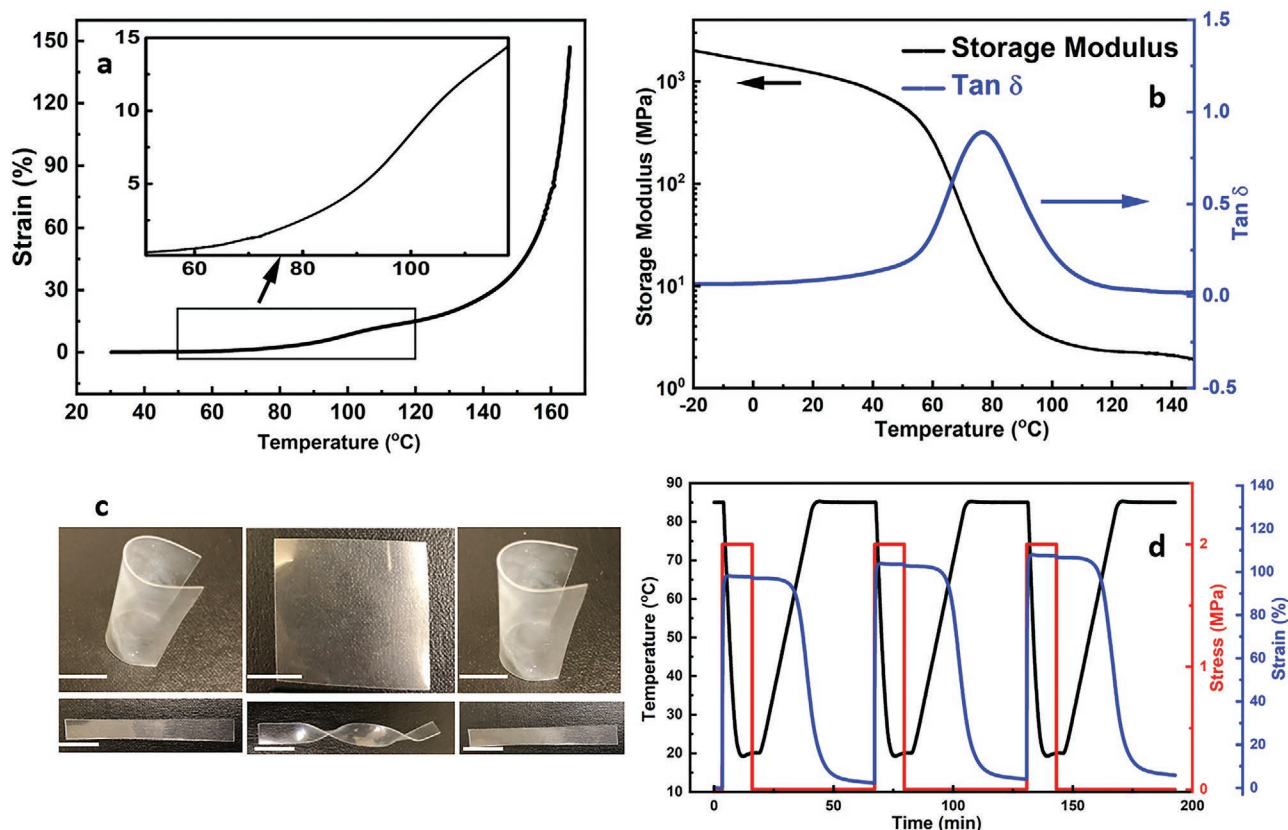

Figure 2. a) Temperature-dependent creep test of PUU-1 under constant force; b) dynamic mechanical analysis of PUU-1; c) visual demonstration for dual-shape memory performance of PUU-1; the reshaped PUU thermoset from Figure 1f and a ribbon were deformed at 85 °C and fixed at RT, and after that the specimens transferred back to their permanent shapes when heated up to 85 °C; d) quantitative test for dual-shape memory performance of PUU-1 (scale bar = 1 cm).
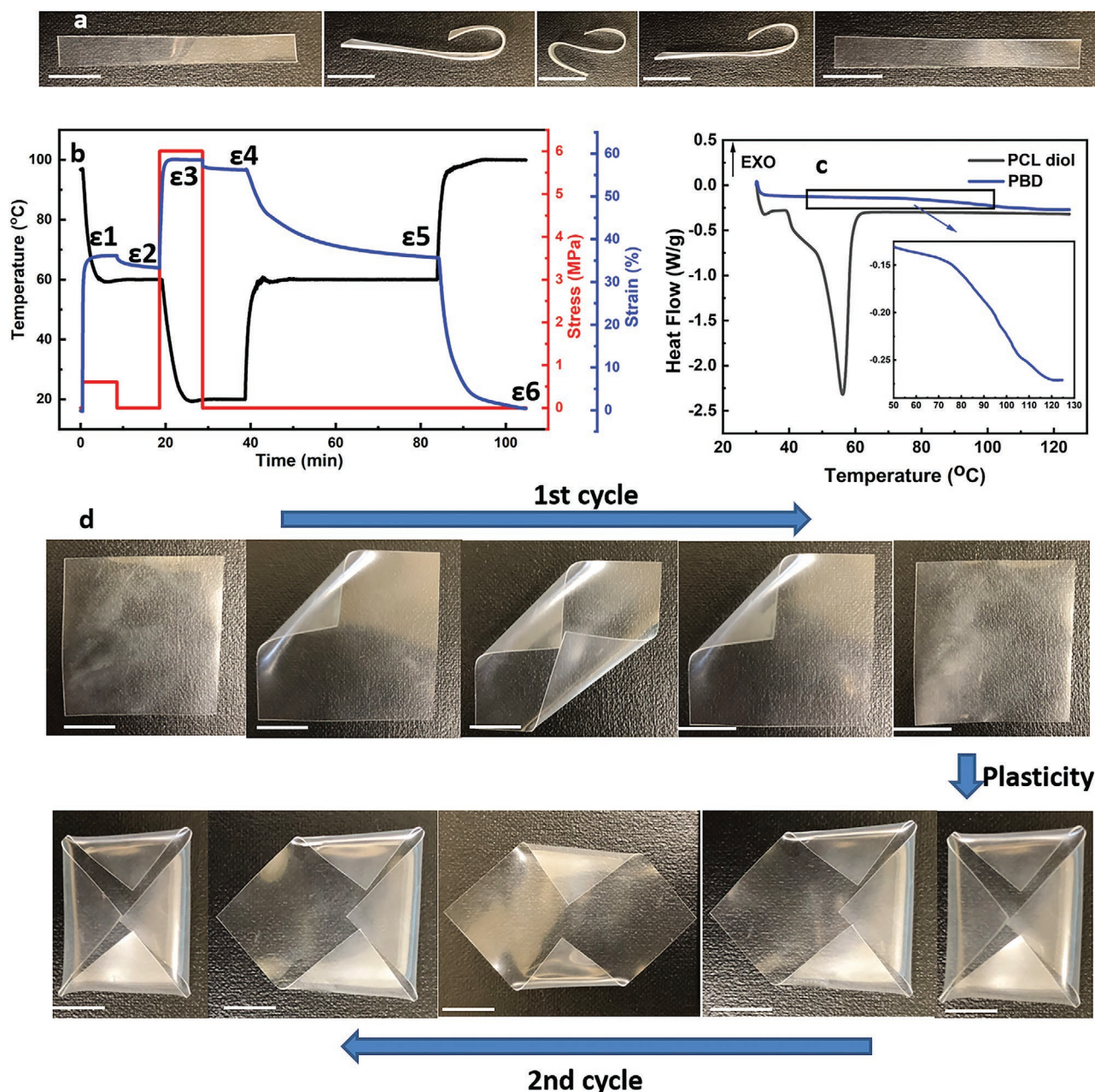
Figure 3. a) Visual demonstration for triple-shape memory behaviors of PUU-1: the specimen was deformed at 100 °C and fixed at 60 °C. After this, it was deformed again at 60 °C and fixed at RT. The specimen transferred back to the first temporary shape when heated up to 60 °C and transferred back to permanent shape when heated up to 100 °C. b) Quantitative test of triple-shape-memory performance of PUU-1. c) DSC curves of PCL diol and PBD. d) The plasticity and triple-shape-memory behaviors of PUU-1. After exhibiting the 1st triple-shape-memory cycle, the specimen can be reshaped at 150 °C for 10 min and then exhibit another triple-shape-memory cycle (scale bar = 1 cm).

was heated up to 100 °C again, it went back to the permanent shape. The first and second temporary shapes have shape fixity ratio of 92.5% and 96.3%, respectively (Figure 3). After fixing the second temporary shape and reheating to 60 °C, the strain recovered to 35.7% (recovery ratio = 90.0%), which was very close to the first temporary shape (strain = 33.3%), indicating the accurate intermediate shape control of this triple-shape-memory PUU. Ultimately, the shape recovered

to its permanent shape with a high recovery ratio of 98.8% when heated up to 100 °C. It should be noted that to create the second temporary shape, the fix temperature for first temporary shape should be still higher than onset glass transition temperature; thus, the fixity ratio of first temporary shape is not easy to be high[5,21b] because the movement of molecular chains are still not totally fixed. Here, the as-designed PUU networks are the chemical integration of two distinct kinds of

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moieties: rigid urea segments (poly (BIMCH-DTBEA), PBD, the synthesis can be found in Supporting Information) with lots of benzene rings and soft PCL chains. DSC test shows that the melting point of PCL diol is 56.6 °C and the PBD has an endothermic behavior at 80–110 °C (Figure 3c), which respectively corresponds to the segment movement of soft and rigid chains in the thermoset networks. Even though 60 °C is higher than the onset glass transition temperature, it is lower than the activation temperature of urea segments. Thus, the first temporary shape can be well fixed by the urea segments without external force.

The permanent shapes play critical roles in SMPs' applications. Considering the crosslinking nature of thermoset, the permanent shape is difficult to be tuned or processed. Thanks to the dynamic nature of HUBs, the PUU crosslinked networks can be reshaped to another permanent shapes via the topological and spatial reconfiguration of HUBs and molecular chains, which integrates the reconfigurability and triple-shape-memory performance into one crosslinked network. As shown in Figure 3d, after exhibiting triple-shape-memory performance, the PUU film was folded and subjected to 150 °C while keeping the external force. After 10 min, the inner stress fully relaxed and the second permanent shape was successfully created, indicating that instead of having to cure the thermoset in a mold with desired shape, the incorporation of HUBs can decouple the synthesis and shape-forming steps of thermoset, which is a huge advantage for the processing of thermoset materials. After that, the PUU-1 could still present triple-shape-memory behaviors. It should be noticed that although the first deforming temperature (100 °C) may cause mild relaxation (plastic deformation), the characteristic relaxation time (36.4 min at 100 °C, calculated from Arrhenius curve) is long enough to allow fast deforming and then quenching to 60 °C, and the final shape recovery was not noticeably deteriorated (Figure 3b). Therefore, the as-designed PUU is a thermoset that combines both plasticity to reshape at high temperature and dimension stability within the temperature range of triple-shape-memory behaviors.

3. Conclusion

In summary, we designed and prepared a reconfigurable PUU thermoset based on HUBs, and the PUU thermoset presented excellent triple-shape-memory performance. The chemical dissociation and reforming of dynamic urea domains endowed the crosslinked networks with fast reconfigurability under high temperature, making the crosslinked SMPs' permanent shape re-designable, which is significant to the practical application of SMPs. In the perspective of materials design, HUBs are very easy to be introduced into any polyurethane systems and the properties of polyurethane can be widely tuned via selecting of commodity and diverse monomers, which is extremely significant to the practical application. Considering the design flexibility, low cost of the raw materials, simple preparation, and fast reconfigurability of HUBs, the as-developed dynamic PUU will be a great platform for designs and commercial scale-up of advanced SMP materials in the future.

Conflict of Interest

The authors declare no conflict of interest.

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