Author Manuscript

Title: Trans-Carbamoylation Enabled Intrinsic Plasticity for Thermoset Shape Memory Polyurethane

Authors: Ning Zheng; Zizheng Fang; Weike Zou; Qian Zhao; Tao Xie

Trans-Carbamoylation Enabled Intrinsic Plasticity for Thermoset Shape Memory Polyurethane

Ning Zheng, Zizheng Fang, Weike Zou, Qian Zhao*, Tao Xie*

Abstract: Thermoset polymers are known for their superior thermo-mechanical performances, but their chemical crosslinking nature typically leads to the intractability. This is reflected in the stark contrast between thermoset and thermoplastic shape memory polymers with the former exhibiting robust shape memory performances but its inability to redefine the permanent shape. Contrary to current knowledge, we reveal here that a classical thermoset shape memory polyurethane readily exhibits an ability in permanent reshaping (plasticity) via trans-carbamoylation enabled network topological rearrangement. By employing a Jianzhi technique (also known as kirigami), we demonstrate unexpected shape shifting versatility for such an otherwise classical material. Since the essential carbamate bond in polyurethanes is one of the most common polymer building units, we anticipate that our finding will lead to enormous benefits in the future beyond shape shifting.

Shape memory polymer (SMP) is a class of smart material capable of fixing temporary programmed shapes and recovering to its permanent shape upon external stimulation.[1] Although polymer shape memory behavior has been known for over half a century, intense interests have only been stimulated in the last decade due to the emergence of a variety of high value added engineering applications including biomedical devices, deployable aerospace structures, and functionally tunable devices. At the fundamental level of material behaviors, the recent discovery of multi-shape memory[2] and reversible shape memory effects[3] has further fueled the explosive growth. Regardless of the complexity of the shape memory behaviors, enabling such properties generally requires the combination of cross-linking and reversible thermal transition. Chemical crosslinking leads to thermoset SMP with robust shape memory behaviors but comes at a cost of losing reprocessability. In contrast, physical crosslinked SMPs can be reprocessed, but often suffer from compromised shape fixity and recovery. A prime example reflecting such a dilemma is shape memory polyurethanes (SMPU). Thermoplastic SMPU represents one of the earliest studied SMPs with their hard and soft domains serving as the physical crosslinkers and thermo-reversible shape memory transition, respectively.[4] Despite its inferior performance relative to its thermoset counterpart, its reprocessability has sustained the interest on this class of materials for many years. In contrast, thermoset polyurethane chemistry has also been widely used in SMP design due to the versatility of the chemistry and the robustness of the resulting materials. However, it is generally understood that thermoset polyurethane cannot be reprocessed, or in the context of shape

memory, the permanent shape of classical thermoset SMPU cannot be altered.

In the general area of polymer materials beyond SMP, resolving the dilemma between thermosets and thermoplastics has historically attracted significant attention. The recently emerged concept of vitrimers is particularly noteworthy.[5] The concept relies on triggering transesterification reactions in a thermoset to allow network topological rearrangement for reprocessing. However, network reformulation to introduce a sufficient amount of ester linkages in the network is needed. Nevertheless, this mechanism has since been extended to various systems based on other exchangeable reactions including siloxane equilibrium,[6] olefin metathesis,[7] and boronic ester exchange.[8] Whereas the vitrimer concept emphasizes more on thermally activated bond exchange, photo-activation via addition-fragmentation chain transfer reaction[9] or disulfide bond exchange[10] also permits network rearrangement for permanent thermoset reshaping. Overall, thermoset reprocessing or reshaping via exchangeable bonds holds great promise but it generally requires delicate network reformulation, which often prohibits their practical potential.

Polyurethane thermosets represent a class of materials with important industrial applications. Intriguingly, their essential carbamate bonds are known to be exchangeable yet the reprocessibility of thermoset polyurethanes has been found to be rather "sluggish".[11] Presumably, this is the very reason why the reversible nature of carbamate bonds has been largely neglected despite their importance as the common polymer building units and the ever-increasing interest on reversible covalent bonds.[12] Nevertheless, it is generally recognized that unless the primary structures of thermoset polyurethanes are altered, their reprocessing via carbamate-only bond exchange is non-practical. This resonates well with the common belief that the permanent shape of thermoset shape memory polyurethanes (SMPU) cannot be redefined. Contrary to this, we illustrate below that the ability to repetitively reset the permanent shape is an intrinsic attribute for classical thermoset SMPU.

We start with thermoset SMPU with carbamate bonds as the only potentially active structural moieties in the networks, as synthesized by reacting (polyethylene glycol)diol (PEG) and glycerine (GLY) with hexamethylene diisocyanate (HDI) (Figure 1). A common catalyst dibutyltin dilaurate (DBTDL) is also present (0.5, 1, and 2 wt%) in the formulation. All three samples show high gel contents (91.6%, 93.7%, and 94.0%, respectively), confirming their thermoset nature. Differential scanning calorimetry analysis (DSC) and dynamic mechanical analysis (DMA) (Figures S1a and S1b, 1 wt% catalyst unless otherwise noted) show that the network possesses a melting transition around 41 ℃ from the PEG chain segments. Importantly, no other peak can be identified in the DSC curve and a perfect rubbery plateau was observed in the DMA curve. These are features fully expected with the simplest and rather classical thermoset SMPU.

The surprise started when three samples with various catalyst contents were subjected to iso-strain stress relaxation

[*]   N. Zheng, Z.Z. Fang, W.K. Zou, Prof. Q Zhao, Prof. T. Xie State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang University, 38 Zheda Road, Hangzhou, 310027, P. R. China
E-mail: qianzhao@zju.edu.cn, taoxie@zju.edu.cn

Supporting information including experimental section for this article is given via a link at the end of the document.

experiments at 130 ºC. Figure 2a shows that all the samples exhibit complete stress relaxation with faster relaxation corresponding to samples with higher catalyst contents. This suggests that the very catalyst (DBTDL) used in forming carbamate bonds in the polyurethane synthesis also promotes the stress relaxation at the elevated temperatures. The results further imply ideal thermal plasticity,[13] in stark contrast to the well-known sluggish reprocessability for such a system. Clearly, the carbamate exchange reaction, while insufficient for reprocessing, is surprisingly effective towards thermal plasticity via a network topological rearrangement mechanism (Figure 1). We note specifically that Figure 1 shows the generically appliable trans-carbamoylation reaction as the mechanism for the stress relaxation. In principle, a less generic trans-carbamoylation mechanism involving residual hydroxyl groups[11] in the network is also possible. However, a detailed study presented in the supporting information suggests that this latter mechanism is negligible for the current system.

PU Precursors

Exchange Reaction

Elasticity and Plasticity Mechanism

I. Plasticity
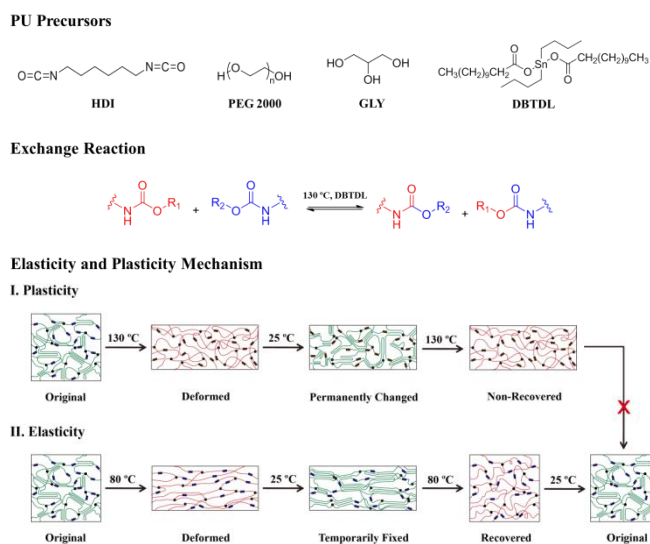
II. Elasticity

Figure 1. Design of the shape memory polyurethane network and mechanistic illustration of its elasticity/plasticity. Black dots: permanent crosslinking points; green lines: frozen chain segments; red lines: activated chain segments; blue blocks: carbamate bonds at their non-activated state; brown blocks: carbamate bonds at their activated state.

The topological rearrangement via bond exchange in response to an external stress leads to a network with no chain conformation change. Thus, the system maintains its highest entropic state and the deformation cannot be recovered due to the lack of entropic driving force (plasticity). We emphasize that stress relaxation alone does not establish plasticity. In fact, stress relaxation behavior is quite common for polymers. Typically, however, stress relaxation cannot reach zero and is often associated with chain conformation change instead of plasticity based on the topological rearrangement.

Herein, the plasticity is opposite to the elasticity based shape memory well known for such a thermoset SMPU. In an elasticity cycle (Figure 1), the external stress is applied at a temperature at which the chain segmental mobility is activated

yet the carbamate bond exchange remains inactive, the macroscopic deformation is thus reflected in chain conformation change (entropy change). While such deformation can be temporarily fixed by freezing the chain mobility via cooling, re-activating the chain segments by heating leads to shape recovery driven by the stored entropic energy.
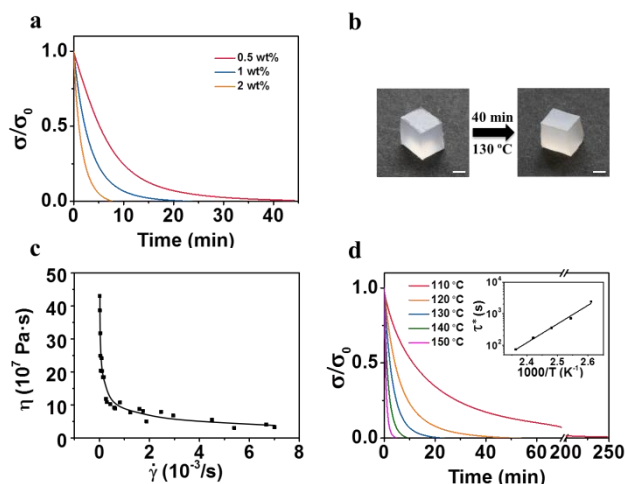
Figure 2. Thermo-mechanical and rheological characterization of the thermoset polyurethanes. a, Stress relaxation behaviors with varying catalyst concentrations at 130 ºC. Strain is 50% and σ and σ_0 represent the instantaneous stress and the initial stress, respectively. b, Illustration of the geometric stability, the bottom half of the cube is slightly distorted due to the gravity acting as the deformation force. (scale bar = 2.5 mm). c, Rheological curve. d, Stress relaxation and Arrhenius analysis of polyurethane from aliphatic diisocyanate.

We note that the plasticity behavior occurs within the rubbery plateau (Figure S1b), indicating that the permanent deformation does not require material flow. The non-flow nature of our system is further confirmed in Figure 2b, showing all the edges of a cubic SMPU sample remains sharp even after extended heating at 130 ºC. Figure S2 further shows that the network behaves as a viscoelastic solid with creep under a constant stress and a large instantaneous strain recovery after the stress is removed. The viscosity can be calculated from creep experiments (see Supporting Information). As such, a rheological curve (Figure 2c) can be constructed by varying the stress in a set of creep experiments. At the initial low strain rate range, the viscosity (within a range of $1-4.4\times10^8$ Pa•s) decreases sharply with the increase of strain rate. Beyond this, the viscosity becomes only slightly dependent on the strain rate with an equilibrium value around 4×10^7 Pa•s. Such a viscosity range places it roughly in line with asphalt (10^6-10^8 Pa•s) and is at least 2-3 orders of magnitude higher than typical polymer melts (10^3-10^5 Pa•s). For further reference, typical glassy polymer has a viscosity of 10^{12} Pa•s. Qualitatively, the rheological behavior is also drastically different from polymer melts which typically show a constant viscosity at low strain rates and gradual viscosity change at higher strain rates. We believe that the unique rheological behavior originates from the dynamic covalent crosslinked nature of the network. We call this dynachemo-rheology in distinction to chemo-rheology used to

describe the irreversible forming of covalent linkages in reactive blends. Herein, the bond breakage and reformation plays a central role in the dynachemo-rheology. The former is not dependent on diffusion whereas the latter via exchange is as it involves two reactive species. Therefore, the exchange reformation is more time dependent. At the very low strain rate range, the corresponding large timescale favors the exchange bond reformation, thus the network exhibits high effective crosslinking density, corresponding to high viscosity. The large impact of the timescale on the exchange reformation translates into the great viscosity sensitivity. Beyond a critical strain rate, the timescale is too short to favor the diffusion-limited reformation via exchange, thus reformation within the original bonding pairs becomes dominant with the equilibrium shifts towards a lower percentage of bonded pairs. Ultimately, this leads to a much lower viscosity that is relatively insensitive to the strain rate.

a

b
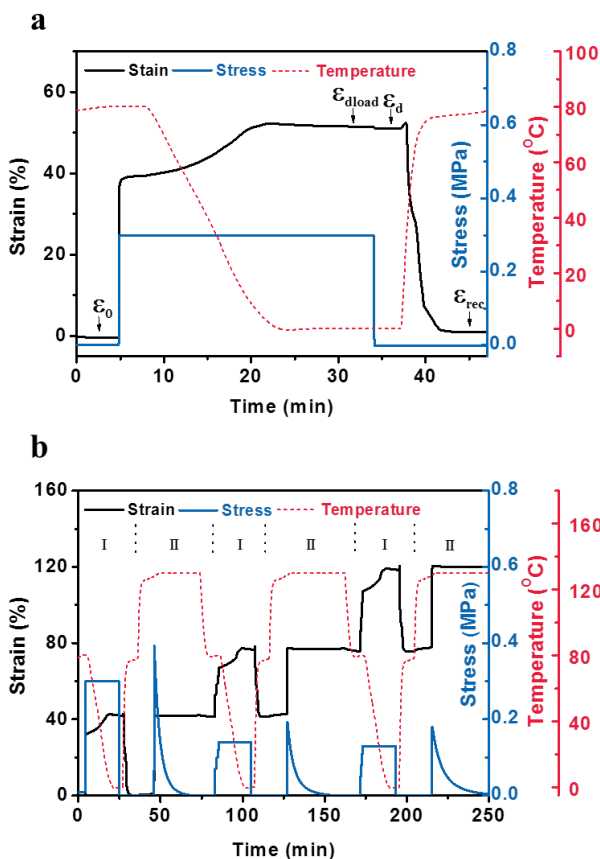
Figure 3. Characterization of the elasticity and plasticity property of the polyurethane thermoset. a, Elastic shape memory cycle. $R_f = \varepsilon_d / \varepsilon_{(dload)} \times 100\%$ and $R_r = (\varepsilon_d - \varepsilon_{rec})/\varepsilon_d$, with ε_0, ε_{dload}, ε_d, and ε_{rec} being the original strain, the maximum strain under load, the fixed strain, and the recovered strain, respectively. b, Consecutive elasticity (labeled I) and plasticity (labeled II) cycles.

Figure 2d shows the temperature dependent stress relaxation behavior with higher temperature promoting faster relaxation, corresponding to an activation energy of 113.6 kJ/mole. In addition to the aliphatic diisocyanate (HDI), aromatic isocyanates are also commonly used for thermoset polyurethane

synthesis. To test the generality of the plasticity, we replaced the aliphatic HDI with an aromatic diisocyanate (4,4'-methylenebis(phenyl isocyanate)) in the formulation. The resulting network exhibits similar plasticity behavior with a higher activation energy of 130.5 kJ/mole (Figure S3). The overall results imply that thermal plasticity is broadly applicable to all thermoset polyurethanes. The discovery is contrary to the current knowledge that classical polyurethane thermosets, like other conventional thermoset polymers, cannot be reshaped permanently, a rather surprising finding given their long history and wide industrial and academic uses.

The plasticity, in combination with the elasticity based shape memory behavior expected for such a network, opens up new opportunities for shape manipulation for this otherwise old and common material. Hereafter, we focus on HDI based thermoset polyurethane. Figure 3a shows the elasticity based shape memory cycle with shape fixity (R_f) and shape recovery (R_r) being 98% and 99%, respectively. The multi-cycling performance (Figure S4) illustrates the robustness, with no visible overall strain shift after four consecutive shape memory cycles. Figure S5 illustrates an opposite plasticity cycle in which the deformation strain is fully and permanently retained after the complete stress relaxation. Collectively, Figures S4 and S5 suggest that the elasticity and plasticity can be realized without any overlap. This further allows achieving multiple elasticity and plasticity based shape manipulation in one combined cycle. The results are presented in Figure 3b, showing three consecutive elasticity/plasticity cycles with near perfect elasticity shape memory and permanent plasticity shape change throughout the entire cycles.
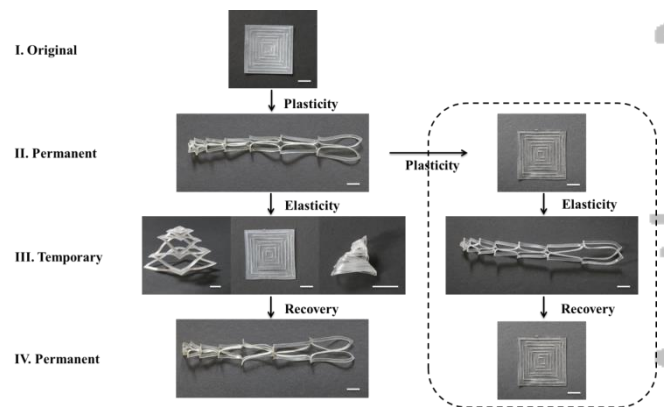
Figure 4. Demonstration of complex shape manipulation via a Jianzhi technique (scale bar = 5 mm).

The on-demand characteristics of the elasticity and plasticity unleashes previously unknown freedom in shape manipulation for this otherwise rather "plain" SMPU. In particular, we resort to a Jianzhi (aslo known as kirigami) technique for shape manipulation. As shall be seen below, Jianzhi requires minimal mechanical interference versus origami that often requires extensive manual folding.[13] Such a distinction is non-trivial as it allows the technique to be extended to the creation of increasingly small structures. As shown in Figure 4, the original shape is a square film with through-line patterns. The line

patterns allow shape manipulation using the Jianzhi technique. As such, the sample can be plastically deformed into a permanent elongated three dimensional shape by simply applying a stretching force followed by annealing at 130 ºC. This permanent shape can be fixed elastically into various temporary shapes including a pyramid, a twisted pyramid, and a flat film. All these temporary shapes can recover fully to the permanent shape. Importantly, this permanent shape can be further deformed plastically back into the original flat square, which can also be fixed into recoverable temporary shapes (right column in Figure 4). Videos showing the various shape changing events above can be found in the Supporting Information. We emphasize here that the unique dynachemo-rheology is essential for the complex shape changing behavior described above. Its high viscosity as well as the strain rate sensitivity allow easy permanent deformation in the direction of the deformation stress while preserving the dimensions in all other directions. We note further that the Jianzhi technique that has shown great promises towards intriguing engineering applications[14] and the extra shape changing capability demonstrated here opens up enormous opportunities.

In summary, we reveal surprising thermal plasticity for classical thermoset SMPU. This behavior arises from the carbamate-only bond exchange and is thus generally applicable to all thermoset polyurethanes. The discovery is contrary to our current understanding and indeed rather unexpected given the long history for this type of materials. The combination of the elasticity and plasticity, along with the extra freedom from the Jianzhi technique, allows highly sophisticated shape manipulations that could enable a wide variety of future engineering applications.
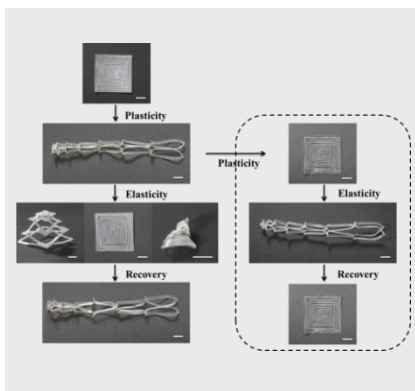
Acknowledgements

Keywords: shape memory, plasticity, polyurethane.

[1] Q. Zhao, H. J. Qi, T. Xie, *Prog. Polym. Sci.* **2015**, 49-50, 79-120; b) M. Behl, M. Y. Razzaq, A. Lendlein, *Adv. Mater.* **2010**, 22, 3388-4100; c) P. T. Mather, X. F. Luo, I. A. Rousseau, *Annu. Rev. Mater. Res.* **2009**, 39, 445-471; d) T. Xie, *Nature* **2010**, 464, 267-270; e) R. R. Kohlmeyer, P. R.

Buskohl, J. R. Deneault, M. F. Durstock, R. A. Vaia, J. Chen, *Adv. Mater.* **2014**, 26, 8114-8119; f) M. Behl, K. Kratz, J. Zotzmann, U. Nochel, A. Lendlein, *Adv. Mater.* **2013**, 25, 4466-4469; g) J. Zhou, S. A. Turner, S. M. Brosnan, Q. X. Li, J. M. Y. Carrillo, D. Nykypanchuk, O. Gang, V. S. Ashby, A. V. Dobrynin, S. S. Sheiko, *Macromolecules* **2014**, 47, 1768-1776; h) Y. Liu, J. K. Boyles, J. Genzer, M. D. Dickey, *Soft Matter* **2012**, 8, 1764-1769.

[2] T. Xie, *Nature* **2010**, 464, 267-270.

[3] a) M. Behl, K. Kratz, J. Zotzmann, U. Nochel, A. Lendlein, *Adv. Mater.* **2013**, 25, 4466-4469; b) J. Zhou, S. A. Turner, S. M. Brosnan, Q. X. Li, J. M. Y. Carrillo, D. Nykypanchuk, O. Gang, V. S. Ashby, A. V. Dobrynin, S. S. Sheiko, *Macromolecules* **2014**, 47, 1768-1776.

[4] a) W. M. Huang, B. Yang, Y. Q. Fu, *CRC Press* USA **2011**; b) S. J. Chen, J. L. Hu, H. T. Zhou, S. G. Chen, *J. Mater. Sci.* **2011**, 46, 5294-5304.

[5] a) D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, *Science* **2011**, 334, 965-968; b) M. Capelot, M. M. Unterlass, F. Tournilhac, L. Leibler, *Acs Macro Letters* **2012**, 1, 789-792; c) J. P. Brutman, P. A. Delgado, M. A. Hillmyer, *ACS Macro Letters* **2014**, 3, 607-610; d) Z. Pei, Y. Yang, Q. Chen, E. M. Terentjev, Y. Wei, Y. Ji, *Nat. Mater.* **2014**, 13, 36-41; e) P. Taynton, K. Yu, R. K. Shoemaker, Y. H. Jin, H. J. Qi, W. Zhang, *Adv. Mater.* **2014**, 26, 3938-3942; f) Z. Pei, Y. Yang, Q. Chen, Y. Wei, Y. Ji, *Adv. Mater.* **2016**, 28, 156-160.

[6] P. Zheng, T. J. McCarthy, *J. Am. Chem. Soc.* **2012**, 134, 2024-2028.

[7] Y. X. Lu, F. Tournilhac, L. Leibler, Z. Guan, *J. Am. Chem. Soc.* **2012**, 134, 8424-8427.

[8] O. R. Cromwell, J. Chung, Z. Guan, *J. Am. Chem. Soc.* **2015**, 137, 6492-6495.

[9] T. F. Scott, A. D. Schneider, W. D. Cook, C. N. Bowman, *Science* **2005**, 308, 1615-1617.

[10] B. T. Michal, C. A. Jaye, E. J. Spencer, S. J. Rowan, *Acs Macro Letters* **2013**, 2, 694-699.

[11] D. J. Fortman, J. P. Brutman, C. J. Cramer, M. A. Hillmyer, W. R. Dichtel, *J. Am. Chem. Soc.* **2015**, 137, 14019-14022.

[12] a) R. J. Wojtecki, M. A. Meador, S. J. Rowan, *Nat. Mater.* **2011**, 10, 14-27; b) Y. Ying, M. W. Urban, *Angew. Chem.* **2014**, 53, 12338-12343; c) G. Deng, C. Tang, F. Li, H. Jiang, Y. Chen, *Macromolecules* **2010**, 43, 1191-1194; d) H. Z. Ying, Y. F. Zhang, J. J. Cheng, *Nat. Commun.* **2014**, 5, 3218.

[13] Q. Zhao, W. K. Zou, Y. W. Luo, T. Xie, *Sci. Adv.* **2016**, 2, e1501297.

[14] a) T. C. Shyu, P. F. Damasceno, P. M. Dodd, A. Lamoureux, L. Xu, M. Shlian, M. Shtein, S. C. Glotzer, N. A. Kotov, *Nat. Mater.* **2015**, 14, 785-789; b) A. Lamoureux, K. Lee, M. Shlian, S. R. Forrest, M. Shtein, *Nat. Commun.* **2015**, 6, 8092.

COMMUNICATION

Text for Table of Contents

Ning Zheng, Zizheng Fang, Weike Zou, Qian Zhao*, Tao Xie*

Trans-Carbamoylation Enabled Intrinsic Plasticity for Thermoset Shape Memory Polyurethane