Thermoset Shape-Memory Polyurethane with Intrinsic Plasticity Enabled by Transcarbamoylation

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

Abstract: *Thermoset polymers are known for their superior thermomechanical properties, but the chemical crosslinking typically leads to intractability. This is reflected in the great differences between thermoset and thermoplastic shape-memory polymers; the former exhibit a robust shape memory but are not capable of redefining the permanent shape. Contrary to current knowledge, we reveal here that a classical thermoset shape-memory polyurethane is readily capable of permanent reshaping (plasticity) after a topological network rearrangement that is induced by transcarbamoylation. By employing the Jianzhi technique (also known as kirigami), unexpected shape-shifting versatility was observed for this otherwise classical material. As the essential carbamate moiety in polyurethanes is one of the most common polymer building units, we anticipate that our finding will have significant benefits beyond shape shifting.*

Shape memory polymers (SMPs) are smart materials that are capable of temporarily adopting programmed shapes and recovering their permanent shape upon external stimulation.[1–3] Although the shape-memory behavior of polymers has been known for over half a century, it has only received intense interest in the last decade owing 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 behavior, the recent discoveries of multi-shape memory[2] and reversible shape-memory effects[3] have further fueled the explosive growth. Regardless of the complexity of the shape-memory behavior, enabling such properties generally requires the combination of cross-linking and reversible thermal transitions. Chemical crosslinking leads to thermoset SMPs with robust shape memory but comes at the cost of reduced reprocessability. In contrast, physically crosslinked SMPs can be reprocessed, but often suffer from compromised shape fixity and recovery. A prime example reflecting this dilemma are shape-memory polyurethanes (SMPUs). Thermoplastic SMPUs represent one of the earliest studied SMPs, with their hard and soft domains serving as the physical crosslinkers and enabling thermo-

reversible shape-memory transitions, respectively.[4] Despite its inferior performance relative to its thermoset counterpart, its reprocessability has sustained the interest in this class of materials for many years. In contrast, thermoset polyurethanes have also been widely used in SMP design owing 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, that 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] This concept relies on triggering transesterification reactions in a thermoset to enable topological network rearrangements 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 equilibria,[6] olefin metathesis,[7] and boronic ester exchange.[8] Whereas the vitrimer concept focuses more on thermally activated bond exchange, photo-activation through addition–fragmentation chain transfer reactions[9] or disulfide bond exchange[10] also allows for network rearrangements for permanent thermoset reshaping. Overall, thermoset reprocessing or reshaping through the use of exchangeable bonds holds great promise but it generally requires delicate network reformulation, which often prohibits their practical use.
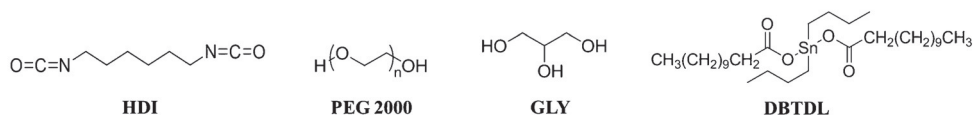
Polyurethane thermosets represent a class of materials with important industrial applications. Intriguingly, their essential carbamate bonds are known to be exchangeable yet the reprocessability of thermoset polyurethanes has been found to be rather poor.[11] Presumably, this is the very reason why the reversible nature of carbamate bonds has been largely neglected despite their importance as common polymer building units and the ever-increasing interest in reversible covalent bonds.[12] Nevertheless, it is generally recognized that unless the primary structures of thermoset polyurethanes are altered, their reprocessing by carbamate-only bond exchange is non-practical. This agrees well with the common belief that the permanent shape of thermoset shape-memory polyurethanes (SMPUs) cannot be redefined. Contrary to this, we illustrate below that the ability to repetitively reset the permanent shape is an intrinsic attribute of classical thermoset SMPUs.

We started with thermoset SMPU with carbamate bonds as the only potentially active structural moieties in the networks, which was synthesized by reacting poly(ethylene
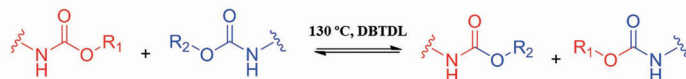
[*] N. Zheng, Z. Z. Fang, W. K. Zou, Prof. Q. Zhao, Prof. T. Xie
State Key Laboratory of Chemical Engineering
College of Chemical and Biological Engineering
Zhejiang University
38 Zheda Road, Hangzhou, 310027 (P.R. China)
E-mail: qianzhao@zju.edu.cn
     taoxie@zju.edu.cn

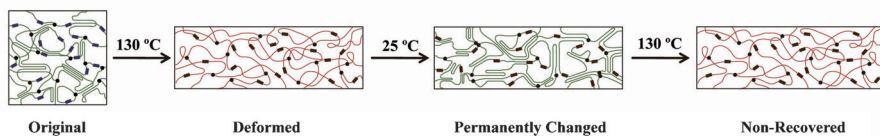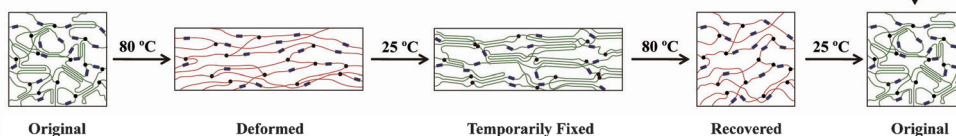Supporting information and the ORCID identification numbers for the authors of this article can be found under http://dx.doi.org/10.1002/anie.201602847.

PU Precursors

HDI   PEG 2000   GLY   DBTDL

Exchange Reaction

130 °C, DBTDL

Elasticity and Plasticity Mechanism

I. Plasticity

Original — 130 °C → Deformed — 25 °C → Permanently Changed — 130 °C → Non-Recovered

II. Elasticity

Original — 80 °C → Deformed — 25 °C → Temporarily Fixed — 80 °C → Recovered — 25 °C → Original

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 in their non-activated state; brown blocks: carbamate bonds in their activated state.

glycol)diol (PEG) and glycerine (GLY) with hexamethylene diisocyanate (HDI; Figure 1). A common catalyst, dibutyltin dilaurate (DBTDL) was also present (0.5, 1, or 2 wt%) in the formulation. All three samples showed 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; see the Supporting Information, Figure S1 a,b; with 1 wt% catalyst unless otherwise noted) showed that the network undergoes a melting transition at about 41°C from the PEG chain segments. Importantly, no other peak could be identified in the DSC curve, and a perfect rubbery plateau was observed in the DMA curve. These are features that are fully in line with the simplest and rather classical thermoset SMPU.

However, rather unexpected results were obtained when three samples with various catalyst contents were subjected to isostrain stress relaxation experiments at 130°C. Figure 2 a shows that all of the samples underwent complete stress relaxation, with faster relaxation times corresponding to samples with higher catalyst contents. This finding suggests that the very catalyst (DBTDL) used for the formation of the carbamate bonds during polyurethane synthesis also promotes stress relaxation at elevated temperatures. These 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 achieving thermal plasticity through a topological network

rearrangement (Figure 1). Figure 1 shows the generically applicable transcarbamoylation reaction as the mechanism of stress relaxation. In principle, a less generic transcarbamoylation mechanism involving residual hydroxy groups[11] in the network is also possible. However, a detailed study suggests that this latter mechanism is negligible for the current system (see the Supporting Information).

The topological rearrangement through bond exchange in response to an external stress leads to a network with no chain conformation changes. Thus the system maintains its highest entropic state, and the deformation cannot be recovered owing to the lack of an entropic driving force (plasticity). We emphasize that stress relaxation alone does not lead to plasticity. In fact, stress relaxation is quite common for polymers. Typically, however, the stress relaxation cannot reach zero, and is often associated with
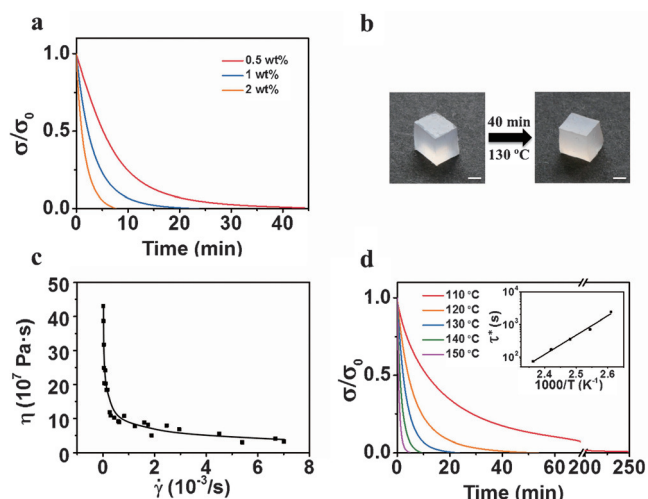
Figure 2. Thermomechanical and rheological characterization of the thermoset polyurethanes. a) Stress relaxation behavior for various catalyst concentrations at 130°C and a strain of 50%. σ and σ_0 represent the instantaneous stress and the initial stress, respectively. b) Illustration of the geometric stability; the bottom half of the cube is slightly distorted with gravity acting as the deformation force (scale bar: 2.5 mm). c) Rheological analysis. d) Stress relaxation and Arrhenius analysis of a polyurethane made from an aliphatic diisocyanate.

chain conformation changes instead of plasticity based on topological rearrangements.

Herein, the plasticity is opposite to the elasticity-based shape memory that is well known for such a thermoset SMPU. In an elasticity cycle (Figure 1), the external stress is applied at a temperature at which the mobility of the chain segments is activated while the carbamate bond exchange remains inactive; the macroscopic deformation is thus reflected in chain conformation changes (entropy change). While such a deformation can be temporarily fixed by decreasing the chain mobility through cooling, reactivating the chain segments by heating leads to shape recovery driven by the stored entropic energy.

Plasticity, on the other hand, was observed within the rubbery plateau (Figure S1 b), indicating that the permanent deformation does not require material flow. This property of our system was further confirmed by the photographs in Figure 2 b, which show that all of the edges of a cubic SMPU sample remained sharp even after extended heating at 130 °C. 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 has been removed. The viscosity can be calculated from creep experiments (see the Supporting Information). As such, a rheological curve (Figure 2 c) can be constructed by varying the stress in a set of creep experiments. At the initial low strain rate, the viscosity (within a range of 1–4.4×10^8 Pa s^{-1}) decreases sharply with the increase in strain rate. Beyond this, the viscosity becomes only slightly dependent on the strain rate with an equilibrium value of around 4×10^7 Pa s^{-1}. Such a viscosity range places it roughly in line with asphalt (10^6–10^8 Pa s^{-1}) and is at least two–three orders of magnitude higher than those of typical polymer melts (10^3–10^5 Pa s^{-1}). For further reference, typical glassy polymers have a viscosity of 10^{12} Pa s^{-1}. Qualitatively, the rheological behavior is also drastically different from polymer melts, which typically show a constant viscosity at low strain rates and gradual viscosity changes at higher strain rates. We believe that the unique rheological behavior originates from the dynamic covalent crosslinked nature of the network. We call this behavior "dynachemorheology" (in contrast to chemorheology) to describe the irreversible formation of covalent linkages in reactive blends. Herein, the breaking and reformation of bonds play a central role in the dynachemorheology. The former is not dependent on diffusion whereas the latter proceeds by exchange as it involves two reactive species. Therefore, the exchange reformation is more time-dependent. At very low strain rates, the corresponding large timescale favors exchange bond reformation, and thus the network exhibits a high effective crosslinking density, which corresponds to high viscosity. The large impact of the timescale on the exchange reformation translates into the great sensitivity of the viscosity. Beyond a critical strain rate, the timescale is too short to favor diffusion-limited reformation via exchange, and reformation within the original bonding pairs thus becomes dominant with the equilibrium shifting towards a lower percentage of bonded pairs. Ultimately, this leads to a much lower viscosity that is relatively insensitive to the strain rate.

Figure 2 d shows the temperature-dependent stress relaxation behavior, with higher temperatures promoting faster relaxation, corresponding to an activation energy of 113.6 kJ mol^{-1}. Aside from aliphatic diisocyanates (e.g., HDI), aromatic isocyanates are also commonly used for the synthesis of thermoset polyurethanes. To test the generality of the plasticity, we replaced the aliphatic HDI with an aromatic diisocyanate, namely 4,4′-methylenebis(phenyl isocyanate), in the formulation. The resulting network exhibited similar plasticity behavior, with a higher activation energy of 130.5 kJ mol^{-1} (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 old and common material. Hereafter, we focus on HDI-based thermoset polyurethane. Figure 3 a shows an elasticity-based shape memory cycle, with shape fixity (R_f) and shape recovery (R_r) values of 98 % and 99 %, respectively. Multiple cycling (Figure S4) illustrates the robustness of this material, with no
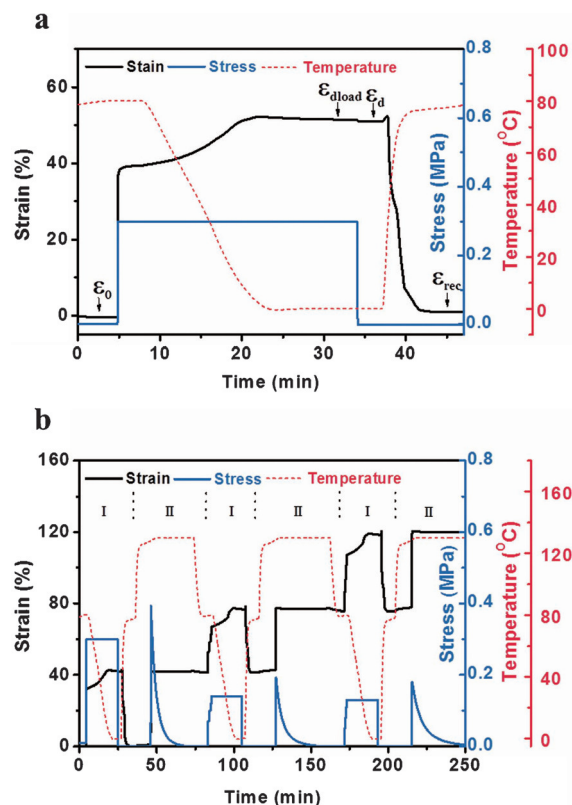
Figure 3. Characterization of the elasticity and plasticity properties of the polyurethane thermoset. a) Elastic shape memory cycle. $R_f = \varepsilon_d / \varepsilon_{(dload)} \times 100\%$ and $R_r = (\varepsilon_d - \varepsilon_{rec}) / \varepsilon_d$, with ε_0, ε_{dload}, ε_d, and ε_{rec} being the original strain, the maximum strain under load, the fixed strain, and the recovered strain, respectively. b) Consecutive elasticity ("I") and plasticity ("II") cycles.
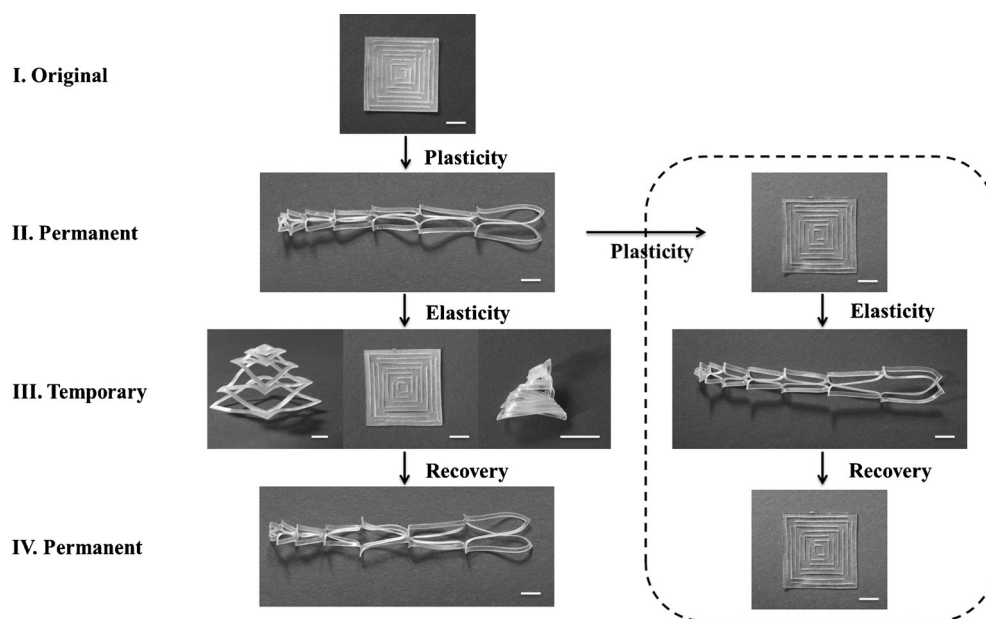
Figure 4. Demonstration of complex shape manipulations according to the Jianzhi technique (scale bar: 5 mm).

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 elasticity and plasticity can be realized without any overlap. This finding further allows for achieving multiple elasticity- and plasticity-based shape manipulations in one combined cycle. These results are presented in Figure 3b, which shows three consecutive elasticity/plasticity cycles with near-perfect elasticity-based shape memory and permanent plasticity-based shape changes throughout all cycles.

The on-demand characteristics of the elasticity and plasticity lead to previously unknown opportunities for the shape manipulation of this otherwise rather "plain" SMPU. In particular, we resorted to the Jianzhi (also known as kirigami) technique for shape manipulation. As shall be seen below, the Jianzhi technique requires minimal mechanical interference whereas origami often requires extensive manual folding.[13] This distinction is non-trivial as it allows for the technique to be used for the fabrication of increasingly small structures. As shown in Figure 4, the original shape is a square film with through-line patterns (the first picture). The line patterns allow for shape manipulation using the Jianzhi technique. As such, the sample can be plastically deformed into a permanently elongated three-dimensional shape by simply applying a stretching force followed by annealing at 130°C. This permanent shape can be fixed elastically into various temporary shapes, including a pyramid, a twisted pyramid, and a flat film. All of these temporary shapes can fully recover the permanent shape. Importantly, this permanent shape can be further deformed plastically back into the original flat square, which can also be fixed into temporary shapes (Figure 4, right column). Videos showing the various shape-changing events can be found in the Supporting Information.

We would like to emphasize that the unique dynache-morheology is essential for the complex shape-changing behavior described above. Its high viscosity as well as the strain rate sensitivity enable easy permanent deformation in the direction of the deformation stress while preserving the dimensions in all other directions. We further note that the Jianzhi technique has shown great promise towards intriguing engineering applications[14] and the extra shape-changing capability demonstrated here opens up enormous opportunities.

In summary, we have revealed that classical thermoset SMPU displays thermal plasticity. This behavior arises from 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 of this type of material. The combination of elasticity and plasticity, along with the beneficial properties of the Jianzhi technique, allows for highly sophisticated shape manipulations that could enable a wide variety of future engineering applications.

[1] a) 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) R. R. Kohlmeyer, P. R. Buskohl, J. R. Deneault, M. F. Durstock, R. A. Vaia, J. Chen, *Adv. Mater.* **2014**, *26*, 8114–8119; e) M. Behl, K. Kratz, J. Zotzmann, U. Nochel, A. Lendlein, *Adv. Mater.* **2013**, *25*, 4466–4469; f) 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, *Polyurethane Shape Memory Polymers*, CRC, Boca Raton, **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 Lett.* **2012**, *1*, 789–792; c) J. P. Brutman, P. A. Delgado, M. A. Hillmyer, *ACS Macro Lett.* **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 Lett.* **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. Int. Ed.* **2014**, *53*, 12436–12440; *Angew. Chem.* **2014**, *126*, 12644–12648; 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.