Shape-Memory Polymers

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A Metallosupramolecular Shape-Memory Polymer with Gradient Thermal Plasticity

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Abstract: *Solid-state plasticity by dynamic covalent bond exchange in a shape-memory polymer network bestows a permanent shape reconfiguration ability. Spatio-selective control of thermally induced plasticity may further extend the capabilities of materials into unexplored domains. However, this is difficult to achieve because of the lack of spatio-control in typical polymer network synthesis. Metal–ligand interactions possess the high strength of covalent bonds while maintaining the dynamic reversibility of supramolecular bonds. Metallosupramolecular shape-memory polymer networks were designed and prepared, which demonstrated solid-state plasticity. The metallo-coordination bonds within these networks permit facile tuning of the plasticity behavior across a wide temperature range, simply by changing the metal ion. By controlling the diffusion of two different metal ions during preparation of a polymer film, a plasticity behavior with a spatial gradient was achieved, providing a unique shape-morphing versatility with potential in shape-memory devices.*

Shape-memory polymers (SMPs)[1] have gained much attention in various application fields; including, medical devices,[2] deployable aerospace structures,[3] and advanced manufacturing.[4] Significant progress has been made in extending the morphing behaviors of SMPs beyond the simplest one-way dual shape-memory behavior.[1] This progress has centered around the reversibility of the morphing,[5] versatility in temporary shape fixing,[6] and new stimulation mechanisms.[7] Innovations involving permanent shapes have been scarce, despite the fact that practical applications often demand complexed permanent geometries. The recently emerged thermal plasticity,[8] which is achieved by dynamic covalent bond exchange in a SMP network, allows fabrication of highly complexed permanent shapes without being limited by traditional molding techniques. Since its discovery, a variety of dynamic covalent bonds have been demonstrated for achieving thermal plasticity in SMPs, including transesterification,[8a] transcarbamoylation,[8c,9] reversible TAD (1,2,4-triazoline-3,5-dione) chemistry,[10] and Diels–Alder reactions.[11]

The above developments pose interesting challenges with respect to the preparation of SMP networks: 1) using non-covalent supramolecular bonds instead of dynamic covalent bonds to achieve thermal plasticity; 2) designing network thermal plasticity in a spatio-selective manner that would further extend the shape morphing versatility. Regarding point one, the challenge lies in the fact that most supramolecular bonds, while intrinsically dynamic, do not simultaneously offer high bond strength and thermal switchability. An exception is the metal–ligand interaction (or metallo-bond),[12] which is not only switchable but also possesses bond strength rivaling typical covalent bonds. Because of these features, metal–ligand interactions have shown distinct advantages in designing self-healing polymers.[12b,13] Additionally, metal–ligand interactions can also be used as the temporary switching segments for SMPs, taking advantage of various mechanisms that can switch the interactions on and off.[7,14] Both self-healing and temporary shape fixing rely on the switching of the metal–ligand interactions. However, there is an important difference that can be easily overlooked. The former requires shifting of the equilibrium to a sufficient extent so that the metallo-network is disintegrated to promote material flow at the damaged sites. In contrast, temporary shape fixing can only be realized at a state in which an integral network structure is maintained while the metallo-bonds are being switched. In principle, plasticity requires that the network situates in between these two states; that is, the equilibrium should be shifted to a state that allows bond exchange and topological change without pushing toward full network disintegration. We hypothesize that this can be achieved by time and temperature control given the dynamic nature of metallo-bonds. Another useful feature of a metallo-bond is that its association–dissociation kinetics are highly dependent on the metal ion,[15] making it potentially useful in designing spatio-selective plasticity if the distribution of metal ions can be controlled. Notably, spatio-selective thermal plasticity is different from photoinduced plasticity;[16] the former is not limited by line-of-sight requirements and is thus more suitable for constructing 3D shapes.

Hereafter, we report our efforts in designing metallo-polymer networks to achieve plasticity in an SMP network. We show that the topological rearrangement kinetics can be tuned by integrating different metal ions in a way that is more convenient than dynamic covalent networks.[9b,17] We further demonstrate that controlling metal ion diffusion during synthesis yields a network with a gradient distribution of metal ions, and consequently gradient plasticity.

The polymer network is illustrated in Figure 1 a. A small amount of terpyridine-containing acrylate (Tpy-A; Table 1) was copolymerized with methyl methacrylate (MMA) and

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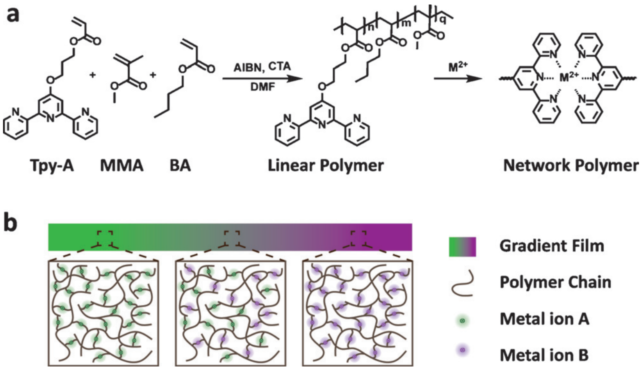

Figure 1. Design of metallosupramolecular networks. a) Network synthesis. b) Spatial distribution of the gradient network. Key: azobisisobutyronitrile (AIBN), chain transfer agent (CTA), *N*,*N*-dimethylformamide (DMF), divalent metal ion (M^{2+}).

butyl acrylate (BA; 3:1 molar ratio) to form a linear polymer. The metal salt was subsequently introduced into a DMF solution of the linear polymer to form a gel. A dry network polymer was obtained by evaporating the solvent. Conceivably, a network polymer possessing a spatial gradient can be obtained by distributing two different metal ions in a gradient-like manner (Figure 1 b). Hereafter, we focus on investigation of networks containing single metal ions. As shown in Table 1, three copolymers (CP1, CP2, and CP3) with similar molecular weights and approximate Tpy molar quantities of 1 %, 2 %, and 3 %, were synthesized. The copolymers demonstrate similar glass transition temperatures around 50 °C. Three metallo-network samples (CP1-Ni, CP2-Ni, and CP3-Ni) were formed by doping stoichiometric amounts of nickel chloride ($NiCl_2$). Other samples doped with different metal ions were prepared and denoted similarly.

The thermal plasticity of the Ni-doped samples was evaluated in stress-relaxation experiments at 100 °C. Figure 2 a shows that complete stress relaxation was observed for all three samples but more time was needed for samples with a higher Tpy content. Specifically, CP1-Ni completes its stress relaxation in 2 min whereas CP3-Ni requires almost 2 h for complete stress relaxation. This is consistent with previous reports that demonstrate a strong correlation between stress-relaxation kinetics and network cross-linking density.[9] Herein, more Tpy in the network corresponds to higher transient cross-linking density at a given temperature, and thus longer time for stress relaxation. Figure 2 b presents the stress-relaxation curves of three samples containing different metal ions (Ni, Fe, and Zn) at 90 °C. Notably, all the metal ions are bivalent and the counterions are chloride. The time for complete stress relaxation for CP2-Zn, CP2-Fe, and CP2-Ni is 4, 18, and 60 min, respectively. The strong dependence of the stress-relaxation kinetics on the type of metal ion implies that different association–dissociation equilibria are associated with each ion.

Table 1: Formulations and characterization of the linear copolymers.

Sample	Tpy content [%] Intended[a]	 Actual[b]	T_g[c] [°C]	M_n[d]
CP1	0.99	0.94	49.6	19420
CP2	1.96	1.92	49.8	20843
CP3	2.91	2.78	50.3	21198

[a] Calculated from monomer feeding ratios in the copolymerization. [b] Calculated from ^1H NMR analyses of the copolymers (Supporting Information, Figure S1). [c] Obtained from differential scanning calorimetry (DSC) analyses. [d] Obtained from gel permeation chromatography (GPC) tests.

We focused on CP2-Ni as a representative sample to further probe the thermomechanical behavior of the SMP network. Figure 2 c shows that complete stress relaxation is achieved at all the temperatures, and that higher temperatures promote fast relaxation. The fast relaxation time of 5 min at 120 °C contrasts sharply with the 60 min required at 90 °C. Using the characteristic relaxation time (τ*),[8] a linear Arrhenius correlation is observed (Figure 2 d), with an activation energy of 54.94 kJ mol^{-1}.

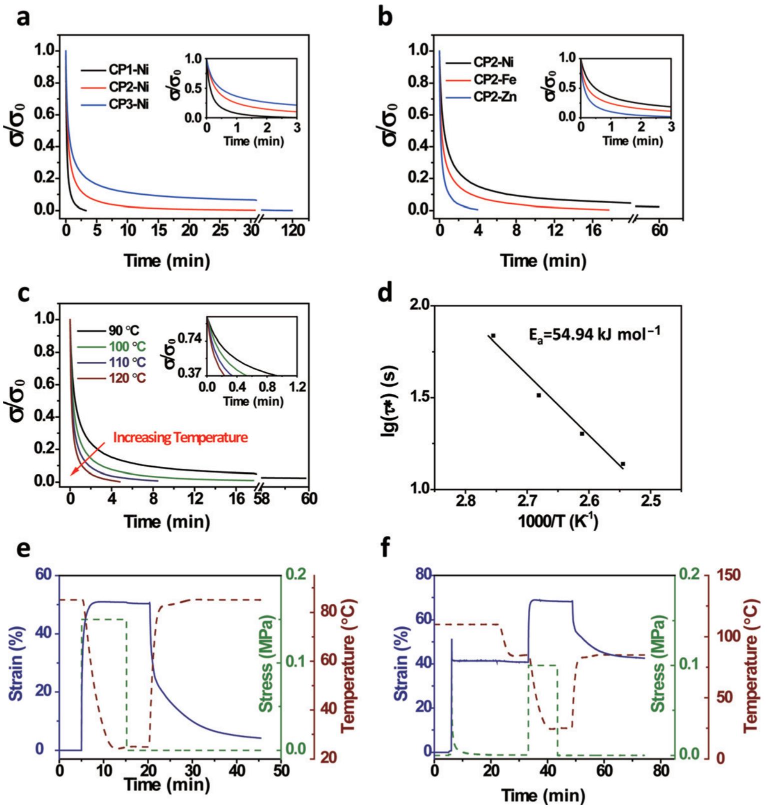

Figure 2. Thermomechanical characterizations of different network samples. a) Stress relaxation of samples doped with Ni ions at 100 °C. b) Stress relaxation of samples doped with different metal ions (Ni, Fe, and Zn) at 90 °C. c–f) Test curves for sample CP2-Ni; including, stress relaxation at different temperatures (c), the Arrhenius curve (d), the shape-memory cycle (e), and the combined plasticity and elasticity cycles (f).

The stress relaxation implies ideal thermal plasticity. The very slow stress relaxation at 90 °C suggests that the network topology can be frozen at a timescale that is relevant for shape-memory experiments (minutes). This, along with the glass transition around 50 °C, suggests that elasticity-based shape-memory behavior can also be expected. The result presented in Figure 2e shows that sample CP2-Ni was uniaxially stretched at 85 °C with pressure (0.15 MPa), the strain was fixed upon cooling to 25 °C, and then recovered at 85 °C under stress-free conditions. The shape fixity (R_f) was 99 % and shape recovery (R_r) was 95 %, confirming an excellent shape-memory behavior. Together, the results in Figures 2c and e suggest that plasticity-based permanent shape reconfiguration and elasticity-based temporary shape fixing can be realized in one combined shape-morphing cycle. Indeed, Figure 2 f illustrates that a plasticity process at 110 °C yields almost perfect shape-reconfiguration behavior, as indicated by full stress relaxation, whereas a follow-on shape-memory process at 85 °C leads to an R_f and R_r of 99 % and 94 %, respectively. Again, this is due to sufficient activation and deactivation of the metallo-bonds at different temperatures. The shape shifting performance in Figure 2 f is quite robust as no deterioration was observed after multiple cycles (Supporting Information, Figure S2). Herein, the high bond strength of the metallo-bonds play an essential role that may be overlooked. They are sufficiently strong to resist strain recovery at room temperature, thereby allowing temporary shape fixing, which is a unique characteristic that many supramolecular bonds (for example, hydrogen bonds) do not possess.

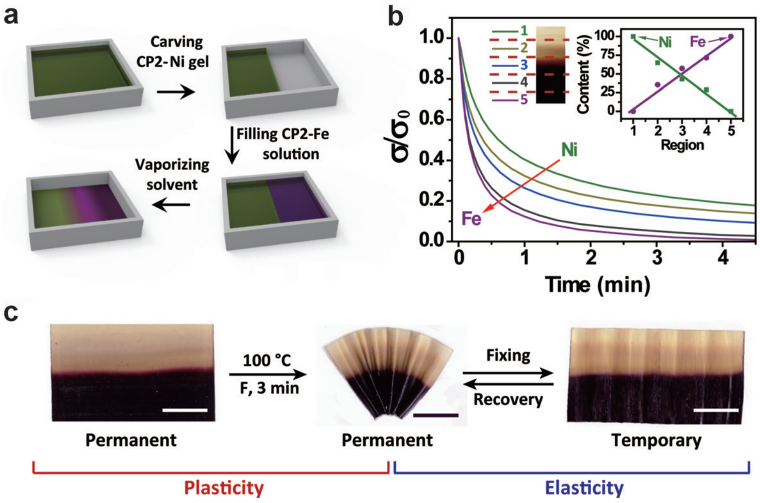

Figure 3. The metallo-shape-memory network with gradient plasticity. a) Fabrication process of the gradient shape-memory sample. b) Gradient distribution of the metal ions and the corresponding stress relaxation behaviors at 100 °C. c) A visual demonstration of shape-shifting versatility arising from elasticity and gradient plasticity; scale bar = 10 mm.

The strong dependence between the metal ions and stress-relaxation kinetics sets the stage for achieving gradient plasticity in a metallo-SMP network. Figure 3a illustrates the sample fabrication process. Half of the CP2-Ni gel swollen in DMF was carved out of a Teflon mold and the resulting empty half was filled in with a DMF solution of CP2-Fe (70 °C), which forms a gel upon cooling. After subsequent removal of the DMF, diffusion of the two metal ions occurred to form a dry metallo-network polymer with a gradient ion distribution. The image in Figure 3b shows that the resulting sample exhibits gradient darkness. Elemental analyses (inset in Figure 3b) confirm that the gradient darkness corresponds to a gradient ion distribution. This further contributes to the gradient stress-relaxation kinetics (Figure 3b); regions that contain more Fe ions exhibit darker color and faster stress relaxation. The gradient sample in a rectangular permanent shape was evenly folded five times in a perpendicular fashion with respect to the gradient direction (Supporting Information, Figure S3) followed by stress relaxation for 3 min at 100 °C. Upon releasing the external deformation force, the fan-shaped permanent shape (Figure 3c) was obtained as a result of the regional variation in stress relaxation. This newly created permanent shape can be further manipulated by elasticity-based shape memory to fix a temporary shape that can be recovered (Figure 3c).

In summary, we have demonstrated that metal–ligand interactions can be utilized as strong, yet dynamically switchable, supramolecular bonds to enable thermal plasticity in an SMP network. This method expands the design of network plasticity beyond dynamic covalent bonds. The versatility of supramolecular metal–ligand interactions provides a unique opportunity to fabricate an SMP network with an ion distribution that possesses a spatial gradient. Since the association and dissociation equilibria of the metal–ligand interaction are strongly dependent on the metal ions, the network with a gradient ion distribution exhibits gradient thermal plasticity. This feature, combined with the elasticity-based shape-memory behavior, introduces new versatility that may be beneficial to future shape morphing devices.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: gradient thermal plasticity · metallosupramolecular networks · polymers · shape-memory · solid-state plasticity

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