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Quantification of Triple-Shape Memory Behavior of Polymers Utilizing Tension and Torsion

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Shape-memory polymers (SMPs) are well investigated smart materials. With their ability to memorize their original shape they are interesting candidates for a large range of applications. Certain SMPs feature triple shape-memory behavior. In these cases, it is possible to fix two different temporary shapes. However, the exact quantification of the individual steps regarding their programming and recovery rate is difficult and has not been possible so far. In this work, a novel approach for the analysis and exact quantification of triple SMPs is presented. By applying a customized rheology protocol, it is possible to perform and to analyze torsional and tensional experiments simultaneously. Consequently, different shapes in different directions (vertical and horizontal) can be fixed and the individual steps can be investigated independently at different switching temperatures.

1. Introduction

Intelligent materials, which are able to show a response to an external stimulus after sensing their environment and/or own state, are a very frequently researched field.[1] These smart materials, in particular polymers, can be useful in many different areas. One promising class is shape-memory polymers (SMPs) with the ability to memorize their original shape. The simplest kind of shape-memory materials features the so-called dual-shape-memory effect. Thus, these materials can fix, under certain conditions, one temporary shape, in which they remain until a certain external trigger is applied leading, subsequently, to the recovery of the former memorized shape.[2]

The shape-memory ability of polymers is not connected to one specific structural element. Rather the whole polymer structure is responsible for that phenomenon. The basic requirements of SMPs are two different structural units.[3,4] One part of the polymer is responsible for stability, whereas the other one is a reversibly switchable moiety. The first one is usually generated by the implementation of netpoints (i.e., stable phase) such as chemical[5] or physical crosslinking, which are mostly used for the preparation of SMPs. In rather special cases, it is possible to utilize interpenetrating networks as stable phase.[6] The second moiety in the polymer is responsible for the fixation of the temporary shape after the programming step. Therefore, reversibility is required.[7] This part of SMPs can be simply generated via crystallization/melting processes[5,8] or glass transitions within the material.[9] However, reversible covalent bonds[10] or supramolecular interactions (for example hydrogen bonds,[11] ionic interactions,[12] or metal-ligand interactions[13–16]) are also potential candidates to generate this phase.

Besides the easiest form of dual SMPs, it is also possible to create polymers, which can fix two (or more) different temporary shapes,[17–20] which are so-called triple (or multiple) SMPs. Herein, starting from the permanent shape (A), the first temporary shape (B) is programmed. Starting from B the second temporary shape (C) can be programmed afterward. If a corresponding trigger is applied, the recovery of the first temporary shape (B) starting from C can be observed. A second trigger, or the same trigger with just a higher intensity, leads to the recovery of the original shape (A) from the intermediate state B. It is possible to use the same kind of trigger, for example, two different switching temperatures; however, two different stimuli can be applied as well.[21]

In contrast to dual SMPs, triple SMPs require two reversible units. For example, it is possible to create a triple SMP using two different thermal transitions, such as two different glass transition temperatures[9] or one crystallization/melting and one glass transition.[9] Other works also showed the possibility to use one very broad glass transition temperature, like found for Nafion.[19]

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Generally, the shape-memory effect can be quantified by the fixity (R_f) and the recovery rate (R_r). The fixity rate quantifies the ability to fix the temporary shape after deformation. Consequently, it represents the ability to store the mechanical energy. The recovery rate indicates the reshaping abilities of the memorized permanent shape and, thus, quantifies the ability to emit mechanical energy.[2] The quantification of the shape memory effect is usually performed via thermo-mechanic-analysis (TMA).[2,4,22] Generally, there are different possibilities for the setup of this method. For dual SMP samples, the test is in all cases easy to perform and leads to realistic and clear results, which are also at different test-setups extremely comparable. The TMA of triple SMPs, however, is much more difficult, caused by the more complex processes. Furthermore, the setup of the measurement has an enormous influence on the triple-shape-memory effect as well as its quantification.[18] Additionally, in the case of two thermal transitions, the boundary between the shape-recovery of each individual step is rather complicated resulting in a poor quantification for each step. Most of the drawbacks of the common TMA investigation of triple-SMPs result from the fact that the same direction is used for both fixation and recovery steps. Thus, also the same measurands are utilized for the evaluation of the individual steps, what makes an independent evaluation of each step almost impossible.

Therefore, a method for the quantification of the triple-shape-memory effect in polymers is presented using different mechanical deformations for each step. More precisely, during the presented TMA measurement one temporary shape is determined via tension while for the deformation of the second torsion is used. This advanced kind of measurement opens the door for investigating the quality of fixation and recovery of both temporary shapes individually in a more detailed fashion.

2. Results and Discussion

The goal of this study was the comparison of the common thermomechanical analysis for the quantification of triple-SMPs and a novel method that enables the investigation of the single processes in a more detailed fashion. Some studies already showed that the common TMA for the quantification of dual SMPs can be also adapted for the investigation of the triple-shape-memory effect.[22] However, the processes are even more complex and the results of this test can therefore be influenced significantly by slight changes in the setup.[23] For example, the manner of the performed heating step(s) during the recovery often strongly affects the determined recovery rates of triple SMPs.[23] The herein presented new method for the characterization of triple-SMPs does not feature these drawbacks and opens the door for a detailed investigation and characterization of that kind of smart polymers.

2.1. Preparation of the Triple-SMP

All tests performed in this study utilized a metallopolymer, which was already reported in a previous study.[14] It was also found that this metallopolymer network features a triple-shape-memory effect. This metallopolymer was synthesized from butyl methacrylate as the main monomer, a methacrylate containing triazole-pyridine ligand (TriazPy-MA, 10%) and triethylenegylcole dimethacrylate (5%) as covalent crosslinker (see **Figure 1**). The polymer was synthesized via free radical polymerization resulting in a covalently crosslinked polymer network (stable phase) that carries ligands in its side chains. Furthermore, zinc(II) acetate was added to the polymer network leading to the formation of reversible *bis*-triazole-pyridine zinc(II)-complexes (first switching unit). Additionally, during differential scanning calorimetry investigations it was found that this metallopolymer network showed a broad glass transition temperature range (30 to 60 °C) which is utilized as the second switching unit.[14] The triple shape-memory ability is shown in Figure 1.

2.2. Dual Shape-Memory

The TMA is an easy and well-known method for the quantification of shape-memory abilities of different materials. During this investigation, the sample is deformed. Therefore, it is possible to use either tension or torsion.[2,22] In general, the sample is heated to or above the switching temperature, twisted or elongated (deformation step), cooled below the switching temperature, while holding the stress (stress-controlled) or the deformation (strain controlled) constant (fixation). Afterward, the stress is removed from the sample, the temperature is raised to or above the switching temperature followed by an annealing step at the same temperature (recovery step).

First, two TMA measurements were performed to investigate the dual shape-memory abilities of the sample at 50 and 90 °C. Temperatures of 90 and 50 °C are those, at which it was possible to fix and recover both temporary shapes during a triple-shape-memory test. Therefore, each step was tested individually. The results of the performed TMAs are displayed in **Figure 2**. The strain was pre-set during the experiments. Starting at the permanent shape (γ_A) and a temperature of 90 °C, respectively 50 °C, the first step was the twisting of the sample until a shear strain (γ) of 25% was reached ($\gamma_{B,load}$). In the next step, the sample was cooled to 25 °C while holding the shear strain constant at 25%. After reaching 25 °C the torsional shear stress was fully removed from the sample leading to the fixed temporary shape (γ_B). Finally, the temperature was raised again to 90 °C, respectively 50 °C followed by an annealing step at this temperature resulting in the recovery of the permanent shape ($\gamma_{A,rec}$). Within this test, it was possible to determine all values required for the calculation of the strain fixity rate (R_f) (Equation (1)), which quantifies the ability of the material to fix the applied deformation, and the strain recovery rate (R_r) (Equation (2)) which represents the quality of the shape-recovery process.

$$R_f = \frac{\gamma_B}{\gamma_{B,load}} \times 100\% \quad (1)$$

$$R_r = \frac{\gamma_{B,load} - \gamma_{A,rec}}{\gamma_{B,load} - \gamma_{A,}} \times 100\% \quad (2)$$

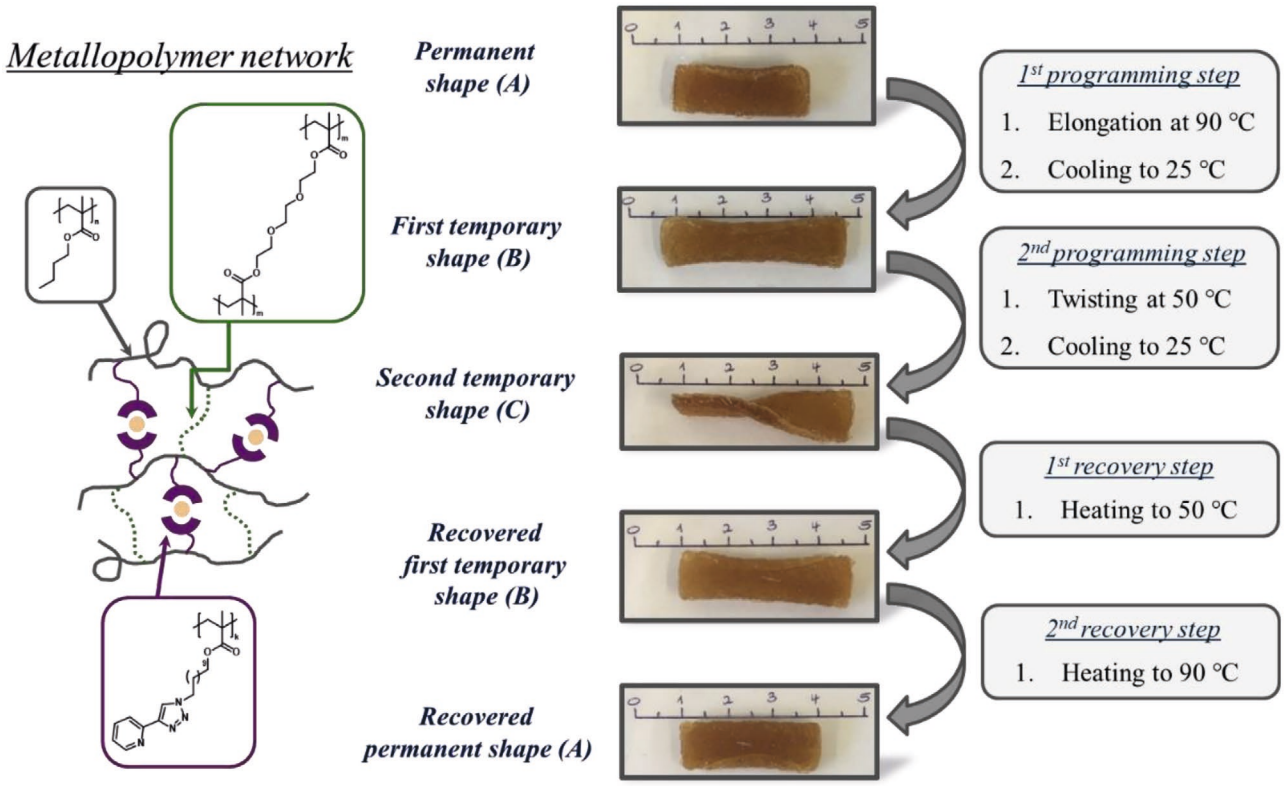

Figure 1. Left: Schematic representation of the structure of the utilized metallopolymer network. Right: Photo series of the triple-shape-memory ability of the metallopolymer networks (Top to bottom: Original permanent shape; first temporary shape, elongated at 90 °C; second temporary shape, twisted at 50 °C; recovered first temporary shape, heating to 50 °C, recovered permanent shape, heating to 90 °C). (Reprinted with permission from reference[14])

These investigations revealed very high fixity rates at both tested temperatures (above 99%). Furthermore, the determined recovery rates were ≈90% indicating a good shape-recovery ability at both investigated temperatures. The determined values for the fixity and recovery rates are summarized in **Table 1**. Applying this test, it could be confirmed that the herein investigated metallopolymer network exhibits very good shape-memory abilities at both switching temperatures. All determined values used for the calculation of the fixity and recovery rate are summarized in Table S1, Supporting Information.

2.3. Common Approach for Triple Shape-Memory

The common approach for the quantification of triple-shape-memory behavior using TMA is based on the method applied for dual shape-memory tests, just with an additional deformation, fixing and recovery step. The disadvantage of this test is that also the same direction is applied for the second deformation. Thus, the polymer sample is either elongated or twisted twice. For a useful and detailed comparison of our later described new approach, which utilizes two different directions for programming of the temporary shapes, we also performed measurements using the classical measurement protocol.

For this purpose, torsion was utilized for the deformation step. Consequently, the sample was twisted for the first shape-memory step and was further twisted for the second step. To show the influence of the testing conditions on the obtained values two measurements were performed with just a slightly different heating program. The results of the performed TMAs are displayed in **Figure 3**. The measurement was performed in a strain-controlled mode. Starting at the permanent shape (γ_A) and a temperature of 90 °C, the sample was twisted until a shear strain (γ) of 20% was reached ($\gamma_{B,load}$). Subsequently, a cooling step to 50 °C followed, while holding the shear strain constant at 20%. Afterward, an annealing step with a full release of the stress at this temperature to fix the first temporary shape (γ_B) followed. Then the sample was further twisted until the torsional shear strain reached 40% ($\gamma_{C,load}$) followed by a further cooling step. At 25 °C, the torsional shear stress was fully removed from the sample leading to the fixed second temporary shape (γ_C). Afterward, the temperature was raised to 50 °C followed by an annealing step at this temperature leading to the recovery of the first temporary shape ($\gamma_{B,rec}$). For the recovery of the permanent shape ($\gamma_{A,rec}$) the sample was heated to 90 °C and annealed at this temperature.

The annealing step at 50 °C during the first recovery step was varied to show the significant influence of such a small change. Thus, the annealing step was performed either for 10 min (Figure 3 top) or for 20 min (Figure 3 bottom).

Furthermore, the *strain fixity rates* (R_f) (Equations (3) to (5)) as well as the *strain recovery rates* (R_r) (Equations (6) to (8)) can

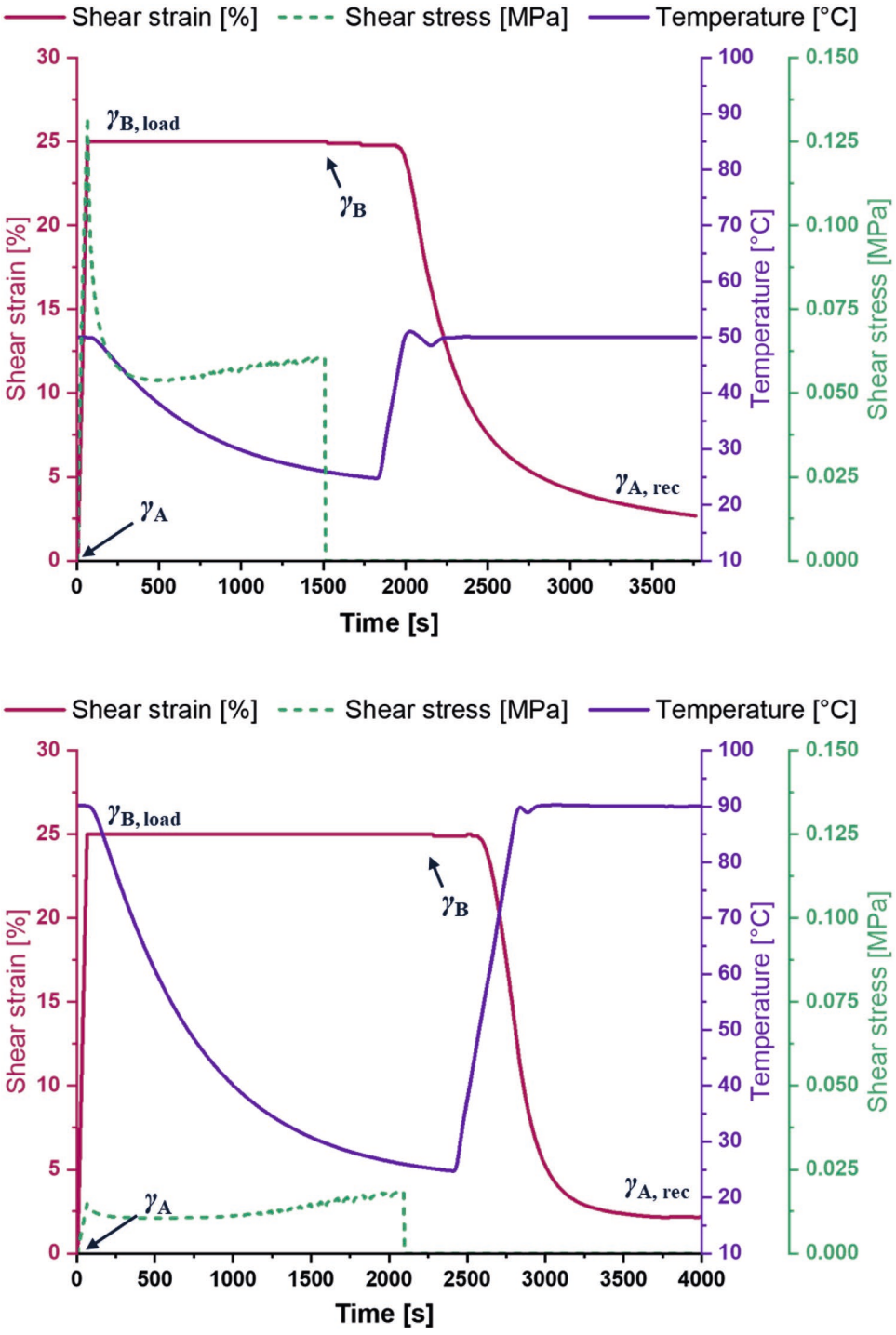

Figure 2. Result of the TMA for the investigation of the dual-shape-memory ability of the utilized metallopolymer network at a switching temperature of 50 °C (top) and 90 °C (bottom).

be calculated for both steps at the two different temperatures. All determined values used for the calculation are summarized in Table S2, Supporting Information.

$$R_{f1}(A \rightarrow B) = \frac{\gamma_B}{\gamma_{B,load}} \times 100\% \quad (3)$$

$$R_{f2}(B \rightarrow C) = \frac{\gamma_C - \gamma_B}{\gamma_{C,load} - \gamma_B} \times 100\% \quad (4)$$

$$R_{f,total}(A \rightarrow C) = \frac{\gamma_C - \gamma_A}{\gamma_{C,load} - \gamma_A} \times 100\% \quad (5)$$

Table 1. Summary of the calculated fixity and recovery rates during the dual shape-memory test based on the results of the TMA performed at different switching temperatures.

	Fixity rate [%]	Recovery rate [%]
Dual 1 (50 °C)	99.2	89.3
Dual 2 (90 °C)	99.6	91.3

$$R_{r1}(C \rightarrow B) = \frac{\gamma_C - \gamma_{B,rec}}{\gamma_C - \gamma_B} \times 100\% \quad (6)$$

$$R_{r2}(B \rightarrow A) = \frac{\gamma_{B,rec} - \gamma_{A,rec}}{\gamma_B - \gamma_A} \times 100\% \quad (7)$$

$$R_{r,total}(C \rightarrow A) = \frac{\gamma_C - \gamma_{A,rec}}{\gamma_C - \gamma_A} \times 100\% \quad (8)$$

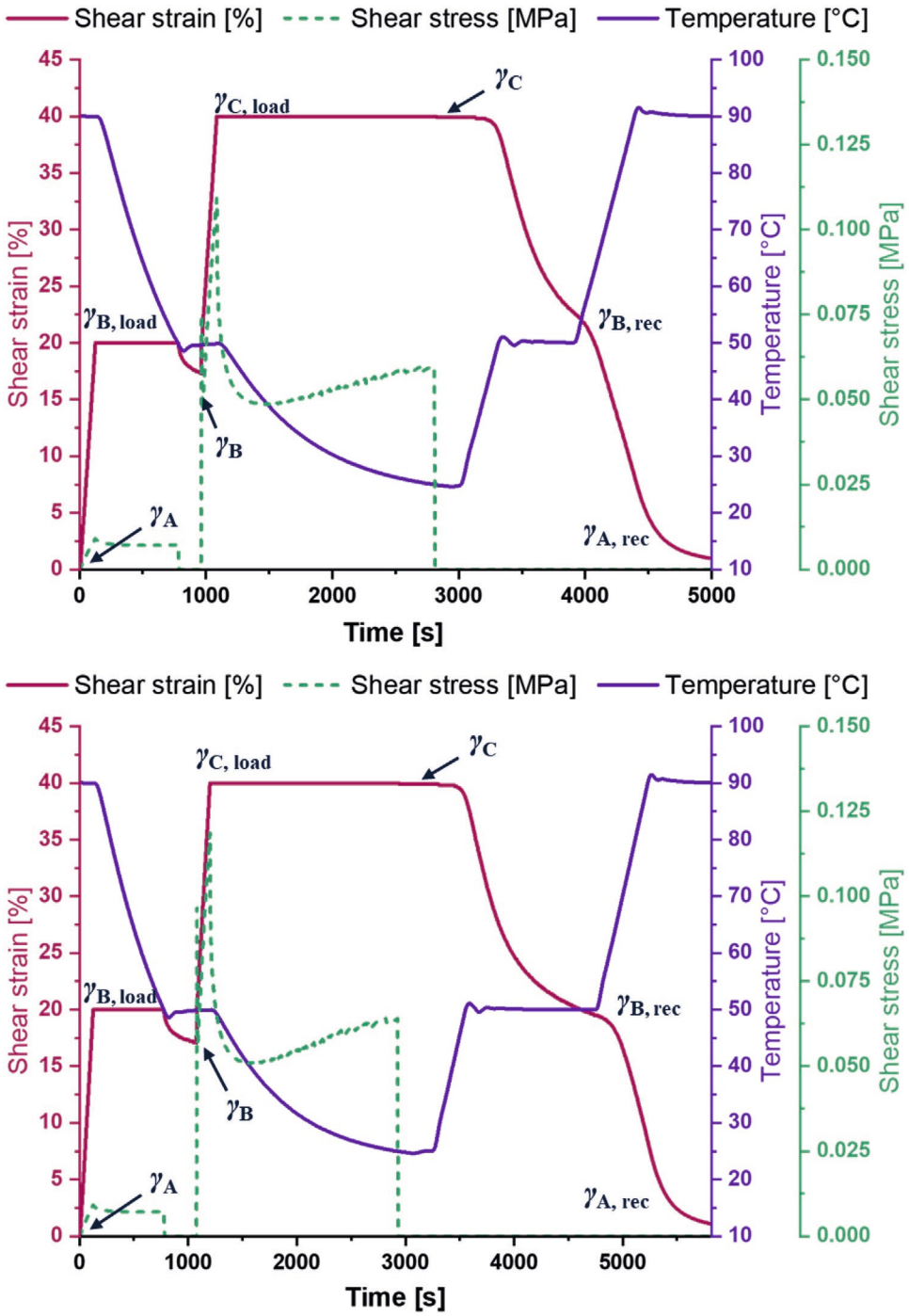

Figure 3. Result of the common TMA for the investigation of the triple-shape-memory ability of the investigated metallopolymer network with a different annealing time at 50 °C: 10 min (top) and 20 min (bottom).

Table 2. Summary of the calculated fixity and recovery rates of the triple-shape-memory metallopolymer network based on the results of the two slightly different TMAs performed on the common way.

	Fixity rate [%]			Recovery rate [%]		
	R_{f1} (Shape A → Shape B)	R_{f2} (Shape B → Shape C)	$R_{f,total}$ (Shape A → Shape C)	R_{r1} (Shape C → Shape B)	R_{r2} (Shape B → Shape A)	$R_{r,total}$ (Shape C → Shape A)
TMA 1 (10 min annealing step for recovery at 50 °C)	86.5	99.6	99.8	75.7	126.0	97.5
TMA 2 (20 min annealing step for recovery at 50 °C)	85.6	99.6	99.8	89.0	108.3	97.3

Using these equations, it was possible to calculate the values for the metallopolymer network, which are summarized in **Table 2**. As it can be seen from the results, it is not ideal that both deformations are performed in the same direction (in our case two times twisted).

Regarding the determined fixity rates, this test revealed realistic values. However, it is not possible to measure the fixity of the first temporary shape during the fixation process of the second one at 50 °C. Consequently, the determined values for R_{f2} could potentially be too high. During the determination of the recovery rates, the significant drawbacks of this kind of measurement get obvious. The calculated values for R_{r2}, which quantifies the ability for the recovery from the first temporary shape (B) to the permanent shape (A), are over 100% and, thus, too high. However, this observation is rather typical for this test.[24,25] The value results from an uncompleted recovery during the first recovery step at 50 °C (second temporary shape (C) to first temporary shape (B)). This remaining strain can then additionally be recovered in the last recovery step at 90 °C leading to unrealistic values above 100%. As a consequence, both recovery steps cannot be isolated from each other disabling a quantification of the individual recovery steps. This phenomenon is particularly observable in cases of a very short annealing step at 50 °C. Thus, a longer annealing time (20 min instead of 10 min) at the first recovery step resulted in a higher recovery rate for the first and a lower one for the second recovery. Nevertheless, the R_r-value is still too high (108%) still showing the disadvantage of the classical method.

2.4. Quantification of the Triple Shape-Memory Effect Using Independently Tension and Torsion

To overcome the drawbacks of the conventional approach, a customized method for the quantification of the triple-shape-memory behavior was developed. In contrast to the common TMA, both shapes are fixed in two different directions (tensile and torsional). This setup enables the investigation of both processes independent from each other caused by the different measurands (use of tension and tension stress for the evaluation of one shape and shear strain and shear stress for the other one). Within this way, the individual steps can be analyzed in detail without any interference from the other recovery step.

The results of the performed TMA are displayed in **Figure 4**. The measurement was performed in tensile and torsional deformation-mode. Starting at the permanent shape (γ_A and ε_A) and a temperature of 90 °C, the sample was elongated leading to a tensile strain (ε) of 43.5% ($\varepsilon_{B,load}$), followed by a cooling step to 50 °C while holding the tensile strain constant. Subsequently, the sample was twisted in a linear ramp at this temperature until a torsional shear strain (γ) of 20% ($\gamma_{B,load}$) was reached. During the programming of the second temporary shape (twisting), the tensile stress was fully removed from the sample and the metallopolymer was able to move in axial direction leading to the first temporary shape (ε_B). In the next step, the sample was cooled to 25 °C while the torsional shear strain was kept constant at 20% followed by an annealing step. During this annealing step, the torsional shear stress was set to 0 Pa to fix the second temporary shape (γ_B). Subsequently, the temperature was raised to 50 °C followed by an annealing step at this temperature for 10 min leading to the recovery of the first temporary shape ($\gamma_{A,rec,\ 50\ °C}$). For the recovery of the permanent shape ($\varepsilon_{A,rec,\ 90\ °C}$) by shrinking, the sample was heated to 90 °C and annealed at this temperature. The complete process can be seen in the Supporting Information (Video S1, Supporting Information).

Due to the different directions for the fixations, it is possible to easily adapt the equations, which are utilized for the dual-shape-memory effect. Consequently, Equations (9) and (10) can be used for the calculation of the fixity and recovery rates for the elongated shape and Equations (11) and (12) for the twisted one. The calculated values are summarized in **Table 3**.

Elongated shape (fixation of the first temp. shape and recovery of the perm. shape)

$$R_{f1} = \frac{\varepsilon_B}{\varepsilon_{B,load}} \times 100\% \quad (9)$$

$$R_{r2} = \frac{\varepsilon_{B,load} - \varepsilon_A}{\varepsilon_{B,load} - \varepsilon_{A,rec,90^\circ C}} \times 100\% \quad (10)$$

Twisted shape (fixation of the second temp. shape and recovery of the first temp. shape)

$$R_{f2} = \frac{\gamma_B}{\gamma_{B,load}} \times 100\% \quad (11)$$

$$R_{r1} = \frac{\gamma_{B,load} - \gamma_A}{\gamma_{B,load} - \gamma_{A,rec,50^\circ C}} \times 100\% \quad (12)$$

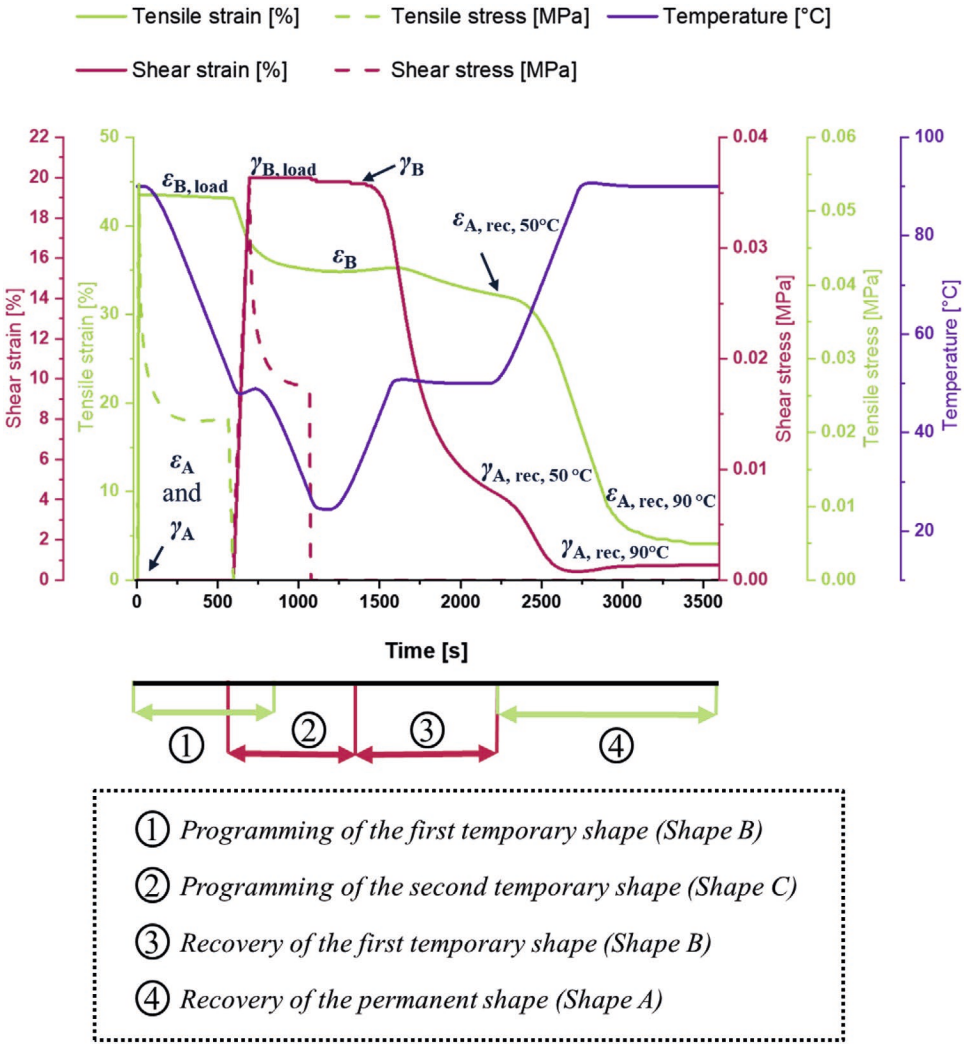

Figure 4. Results obtained from the TMA method for the investigation of the triple-shape-memory ability of the metallopolymer network.

This method permits to calculate the common recovery and fixity rates for the two individual steps more exactly and easier compared to the conventional approach. Besides, it is also possible to study the behavior of the two different deformations during the recovery of the other one. Thus, it can be investigated how the elongated shape behaves during the recovery of the twisted one and vice versa. For example, the further process of the twisted shape, which was not completely recovered at 50 °C, can be monitored during further annealing up to 90 °C. In the conventional approach for the analysis of triple-shape-memory behavior, both steps merge each other and move in the same direction. Therefore, such in-depth studying is not possible. The presented method enables to calculate the recovery rates at the other temperature (Equations (13) and (14))

Recovery of the elongated shape at 50 °C (during recovery of the twisted shape).

$$R_{r1b} = \frac{\varepsilon_{B,load} - \varepsilon_A}{\varepsilon_{B,load} - \varepsilon_{A,rec,50\,°C}} \times 100\% \quad (13)$$

Recovery of the remaining twisted shape at 90 °C (during recovery of the elongated shape).

$$R_{r2b} = \frac{\gamma_{B,load} - \gamma_A}{\gamma_{B,load} - \gamma_{A,rec,90\,°C}} \times 100\% \quad (14)$$

The calculated values for R_{r1b} and R_{r2b} are also listed in Table 3. It can be seen that the twisted shape (second temporary shape), which was programmed at 50 °C, does not completely recover at 50 °C (81%). During further heating to 90 °C, an ongoing recovery step can be observed resulting in a final R_r-value of 96.5%. In contrast, the elongated shape, which was programmed at 90 °C and which should also recover at this temperature, featured already at 50 °C a loss of the programmed shape (recovery of 19%). During a commonly performed measurement, this 19% would also have been attributed to the first recovery step resulting in too high values for the first recovery rate. Thus, the two individual processes can be quantified and analyzed in detail and independently. This permits us to obtain more insights into the recovery behavior of triple-SMPs.

Table 3. Summary of the calculated fixity and recovery rates of the triple-shape-memory metallopolymer network based on the results of the TMA investigation using tension and torsion.

	Tension			Torsion		
	R_{f1} [%] (fix. of elongated shape)	R_{r1b} [%] (shrinking at 50 °C)	R_{r2} [%] (shrinking at 90 °C)	R_{f2} [%] (fix. of twisted shape)	R_{r1} [%] (turnback at 50 °C)	R_{r2b} [%] (turnback at 90 °C)
Novel TMA	80.7	19.3	90.6	99.0	80.8	96.5

However, at the end of the measurement at 90 °C, the sample restored nearly the complete elongated shape and the remaining twisting. The determined values for all calculations are summarized in Table S3, Supporting Information. As an illustration of the entire measurement, a video was taken during the TMA, which is available in Video S1, Supporting Information.

Table 4 presents a detailed comparison of the determined fixity and recovery rates for the different analysis methods. This clearly indicates the drawbacks and inaccuracies of the common way for the investigation of triple-SMPs. Besides the fact that depending on the setup different recovery rates are determined, also the fixity rate of the first temporary shape is too high. Furthermore, a significant deviation was found for the determined recovery rates. Consequently, the herein presented novel method for the quantification of triple shape-memory abilities provides more realistic values.

A comprehensive comparison of the conventional approach method and the presented advanced method is shown in **Figure 5**. In general, the novel method features a lot of advantages compared to the classical one for the quantification of triple shape-memory properties. It enables the opportunity to investigate the fixation and recovery steps of all shapes independent from the other deformation at the same time, which was not possible up to now. Thus, the new method could open the way for a much more detailed investigation of this kind of useful smart polymers. It would also be possible to use this kind of measurement for the investigation of multiple SMPs. However, since the presented method also offers just two directions for the deformation and, thus, not all steps can be studied independently from each other.

3. Conclusion

The current study presents a detailed investigation of the TMA for the quantification of triple shape-memory-polymers. The analysis starts from the investigation of the dual-shape-memory properties up to the presentation of an advanced setup for the thermo-mechanical-analysis. The presented method enables a comprehensive investigation of triple-shape-memory properties of polymers. Furthermore, this work presents a profound comparison of the conventional TMA, which is applied for the quantification of the triple-shape-memory effect. Significant advantages were found for the utilized method. This method enables the investigation of the single shape recovery in tensile and torsional direction independently and, therefore, in a more detailed fashion. Consequently, the undelaying process in triple-SMPs can be analyzed in detail.

4. Experimental Section

Materials and Methods: All chemicals were used as received from TCI (Eschborn, Germany), Sigma Aldrich (Darmstadt, Germany), Alfa Aesar (Kandel, Germany), Thermo Fisher Scientific (Geel, Belgium) and Acros Organics (Geel, Belgium) if not otherwise stated. All solvents were dried over molecular sieve under a nitrogen atmosphere. The used liquid monomers, butyl-methacrylate and tri(ethylene glycol) dimethacrylate, were destabilized over a short AlOx column (neutral AlOx, obtained from Molecula, Darlington, UK).

The synthesis and characterization of the used metallopolymer is described in detail in ref. [14].

Thermomechanical Analysis: The TMA for the investigations of the shape-memory properties (dual shape-memory and the "common" triple shape-memory test) were performed on an MCR 301 rheometer from Anton Paar (Graz, Austria) using the convection oven device CTD 450, which covers a temperature range from –150 to 450 °C. Rectangular samples of ≈30 mm length, 10 mm width and a thickness ranging between 3 and 6 mm were measured using a solid rectangular fixture (SRF) designed for solid samples. After fixing the samples, a free length ranging between ≈15.0 and 16.5 mm resulted in the experiments.

Dual-Shape-Memory Test: After fixing the sample, the temperature was set to 90 °C (respectively 50 °C). Subsequently, a torsional shear strain was applied to the sample at a rate of 25% min^{-1} until a total shear strain of 25% was achieved, corresponding to a deflection angle of 72 degrees. In the following cooling step down to 25 °C (cooling rate: 2 K min^{-1}), the torsional shear strain of 25% was kept constant.

Table 4. Comparison of the determined fixity and recovery rates during the common and the advanced method.

	Fixity rates		Recovery rates	
	R_{f1} [%] (fix. of shape B at 50 °C)	R_{f2} [%] (fixation of shape C at 90 °C)	R_{r1} [%] (recovery of shape B at 50 °C)	R_{r2} [%] (recovery of shape A at 90 °C)
TMA 1 (10 min annealing step for recovery at 50 °C)	86.5	99.6	75.7	126.0
TMA 2 (20 min annealing step for recovery at 50 °C)	85.6	99.6	89.0	108.3
Novel TMA	80.7	99.0	80.8	90.6

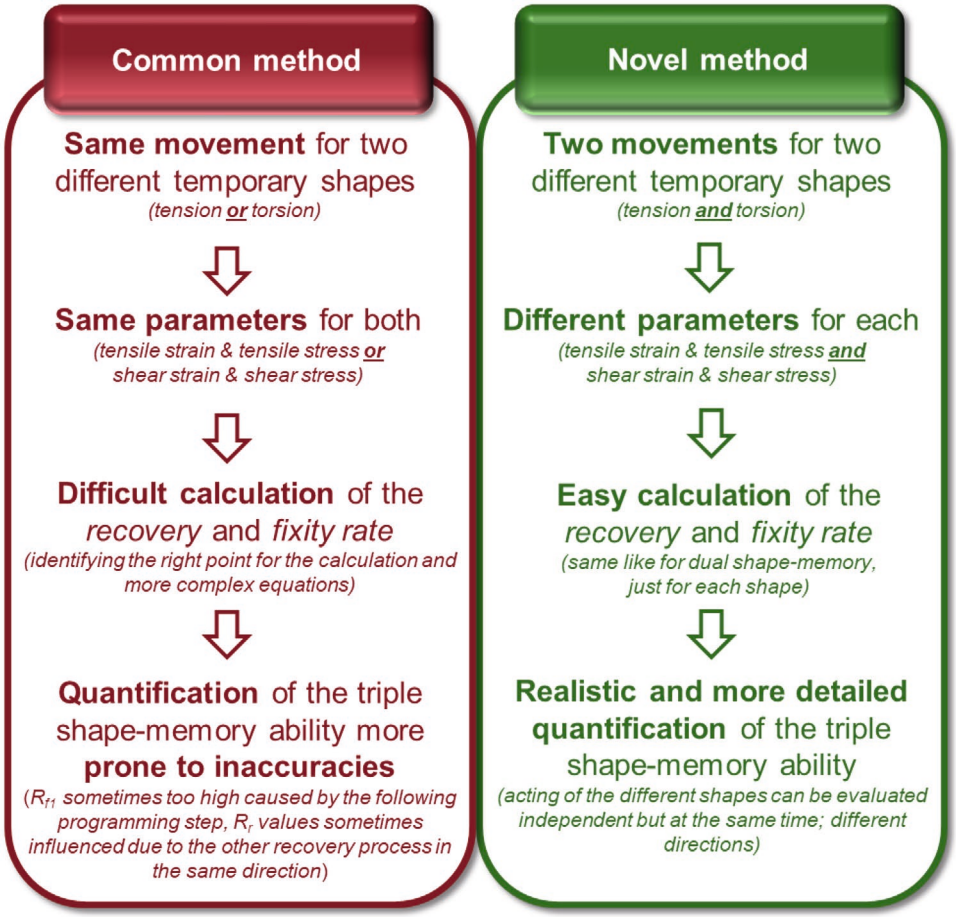

Figure 5. Comparison of the common performed TMA and the TMA using torsion and tension for the investigation of triple-shape-memory polymers.

Afterward, the stress was released from the sample while keeping 25 °C. Finally, the sample was heated again to the initial temperature of 90 °C, respectively 50 °C, (heating rate: 10 K min^{-1}) followed by an annealing step at this temperature.

Common Triple-Shape-Memory Test: After fixing the sample, the temperature was set to 90 °C. Subsequently, a torsional shear strain was applied to the sample at a rate of 20% min^{-1} until a total deformation of 20% was achieved, corresponding to a deflection angle of 36 degrees. In the following cooling step to 50 °C (cooling rate: 2 K min^{-1}), the shear strain of 20% was kept constant. Afterward, at 50 °C, the stress was released from the sample, followed by an annealing step at this temperature. Afterward, a torsional shear strain was applied to the sample at a rate of 10% min^{-1} until a deformation of 40% was reached, corresponding to a deflection angle of 73°. The sample was cooled to 25 °C while holding the shear strain constant at 40%. After the temperature reached 25 °C, the torsional shear stress was fully removed from the sample. The next step was the annealing and, thus, the sample was heated again to 50 °C (heating rate: 10 K min^{-1}). The temperature was kept constant for 10 min (TMA 1) and 20 min (TMA 2), respectively. Finally, the sample was again heated to the initial temperature of 90 °C (heating rate: 10 K min^{-1}) followed by an annealing step.

Triple-Shape-Memory Test: The cyclo-mechanic-test for the analysis of triple-shape-memory abilities was performed on an MCR 702 MultiDrive rheometer from Anton Paar (Graz, Austria) using a convection oven device CTD 180, which covers a temperature range from −20 to 180 °C. A linear drive motor was installed in the MCR 702 MultiDrive for the performance of the cyclo-mechanic-test. This configuration enabled the possibility of running experiments with the upper rotational drive (EC-Motor) in combination with the lower linear drive unit. For this test, it was of particular advantage since a torsional and tensile deformation could be applied on the same sample during the same experiment. Samples of 29.0 mm length, 10.5 mm width, and 4.5 mm thickness were measured using a SRF designed for torsional and tensile measurements, respectively. After clamping the sample, a free length of 18.4 mm was measured. After fixing the sample, the temperature was set to 90 °C. Subsequently, a tensile strain was applied to the sample at a rate of 1 mm s^{-1} until the sample was elongated ≈8 mm, corresponding to a tensile strain of 43.5%. In the following cooling step to 50 °C (cooling rate: 5 K min^{-1}), the tensile deformation was kept constant at the same level. Afterward, the tensile stress was fully removed from the sample. In the next step, a torsional shear strain was applied to the sample at a rate of ≈12% min^{-1} until a deformation of 20% was reached. The sample was able to move in the axial direction since the normal force was set to 0 N (also for all following steps). After the second deformation (torsional), the sample was cooled to 25 °C (cooling rate: 5 K min^{-1}), followed by an annealing step at this temperature while also the torsional shear stress was fully removed from the sample (shear stress set to 0 Pa). Therefore, the sample was able to relax in both directions (axial and torsional). In the next step, the sample was heated again to 50 °C (heating rate: 5 K min^{-1}) followed by an annealing step at this temperature (10 min). Finally, the sample was again heated to the initial temperature of 90 °C (heating rate: 5 K min^{-1}) and annealed for 15 min. The complete process can be seen in the Supporting Information (Video S1, Supporting Information).

The aforementioned test was preset using the software RheoCompass (Anton Paar, Graz, Austria). The videos were obtained and synchronized with the measurement using the same software. The results were exported as csv-files and further processed with OriginPro 2018 (OriginLab Corporation, Northampton, MA, USA).

The results of all thermomechanical analyses as well as a video of the measurement are summarized in the Supporting Information (Tables S1–S3, Supporting Information).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare that Anton Paar develops, produces and sells the rheometer MRC301 and the rheometer MCR 702 MultiDrive. J.A.R.A. is an employee of Anton Paar.

Data Availability Statement

The raw data required can be found under the following link: Meurer, Josefine; Rodriguez Agudo, Jose Alberto; Zechel, Stefan; Hager, Martin; Schubert, Ulrich S. (2020), "Data for: A novel approach for the quantification of triple-shape memory behavior of polymers," Mendeley Data, v1 https://doi.org/10.17632/3f44n8wxn5.1

Keywords

quantification of shape-memory, rheology, shape-memory polymers, thermo-mechanical analysis, triple-shape-memory

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