

The Influence of Programming Conditions on the Triple-Shape Effect of Copolymer Networks with Poly(ω -pentadecalactone) and Poly(ϵ -caprolactone) as Switching Segments

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Summary: A versatile triple-shape material based on the two crystallizable segments poly(ω -pentadecalactone) and poly(ϵ -caprolactone) was synthesized showing triple-shape capability after application of the typical two-step triple-shape creation procedure at elevated temperatures (TSCP) as well as a one-step programming procedure at high temperature or at room temperature by cold drawing. By applying TSCP and varying the sequence of programming temperatures, the influence of the programming procedure on the triple-shape capability was investigated. The application of such a modified TSCP enabled to a certain extent the control of triple-shape capability by influencing the crystallization behavior of the two switching segments in these copolymer networks.

Keywords: polyesterurethanes; polymer networks; shape-memory effect; thermosensitive polymer; triple-shape materials

Introduction

Shape-memory polymers (SMP) and composites thereof are actively moving materials with the ability to change their shape when triggered by an external stimulus.^[1–7] SMP have developed to a technology platform that allows the tailored design of multifunctionality, which comprises additional to the shape-memory effect functionalities such as biodegradability or the ability to load and controllably release drugs.^[8–11] Besides such multifunctional dual-shape polymers recently biodegradable multiphase polymer networks were

introduced, which showed a triple-shape effect.^[12,13] In this paper we report on biodegradable materials being able of switching between three different shapes. Triple-shape polymers are an emerging class of SMP, being able to perform two consecutive shape changes in response to heat.^[5,14–19] These shape changes correspond to the recovery of two different deformations in reversed order, which were programmed before at elevated temperature levels by application of external stress (triple-shape creation procedure, TSCP). Triple-shape polymers can switch from a first temporary shape (A) to a second temporary shape (B) and from there to the permanent shape (C) by subsequent increase of temperature. The thermal transitions associated to the two necessary switching segments can be glass transitions (T_g) or melting points (T_m).

Recently, a triple-shape material based on the two crystallizable segments poly(ω -pentadecalactone) (PPD) and poly(ϵ -caprolactone) (PCL) was synthesized show-

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ing triple-shape capability also after gentle programming procedures applying only one deformation at high temperature or even at ambient temperature.^[12,13] In these PPD/PCL copolymer networks the two switching segments were introduced by hydroxytelechelic star-shaped precursors, which were then crosslinked by a diisocyanate crosslinker in a polyaddition reaction. Copolymer networks with a certain composition show a reversible triple-shape behavior under constant stress, which is based on crystallization induced elongation (CIE).^[20] By determining the triple-shape characteristics of these copolymer networks of different compositions it became evident that the two segments influence each other during crystallization. This influence became apparent in the crystallization temperatures (T_c) determined by DSC measurements. Independently from the cooling rate the PPD segment tends to crystallize from a mixed PPD/PCL fraction near the T_c of the pure PCL segment.^[13] Depending on the weight ratio of the two segments in the copolymer networks, one, two or three T_c could be found. Only a very restricted composition led to the independent crystallization of both segments resulting in a triple-shape effect during cooling under stress (ratio of the segments 50:50 wt%).^[20] After TSCP the triple-shape characteristics such as switching temperature (T_{sw}), relative recovery ($\Delta\varepsilon_{rel}$), recovery ratio (R_r), and the temperature range of each recovery step (ΔT_{rec}) strongly depended on the composition of the respective copolymer network.^[13]

For two different triple-shape materials as well as nano-composites thereof it could be shown, that a modification of the typical two-step TSCP (TSCP1) by changing the sequence of programming temperatures could influence the triple-shape capability.^[19] This new programming method (TSCP2) was applied on copolymer networks based on PCL and poly(cyclohexyl methacrylate) segments (MACL) as well as copolymer networks with a PCL backbone and grafted poly(ethylene glycol) side chains (CLEG). MACL incorporates one

crystallizable and one glassy switching segment, while CLEG consists of two crystallizable switching segments but only one of them contributes to the overall elasticity. In the PPD/PCL copolymer networks both switching segments are crystallizable and contribute to the overall elasticity. TSCP2 could also be used to improve the triple-shape characteristics of PPD/PCL copolymer networks since the triple-shape effect is based on two melting transitions and requires sufficiently separated crystallization processes. We report on the investigation as to which extent the triple-shape effect of these copolymer networks could be influenced by application of TSCP2.

The shape-memory properties of three sets of copolymer networks based on PPD precursors with an average molecular weight (M_n) of 5100 g·mol⁻¹, and PCL precursors with three different M_n were investigated in.^[13] To compare the triple-shape capability after the TSCP2 the set of copolymer networks based on the PCL precursor with $M_n = 9600$ g·mol⁻¹ was chosen since in each of the two other sets one copolymer network was found exhibiting only one crystallization process. Within these set of copolymer networks the mass fraction of the PCL precursor in the network synthesis (μ_{PCL}) was varied between 25 wt% and 75 wt%.

Experimental Part

Preparation of Copolymer Networks

The copolymer networks were based on hydroxytelechelic star-shaped PPD and PCL precursors synthesized by ring opening polymerization. Three arm PPD with $M_n = 5100$ g·mol⁻¹ and four arm PCL with $M_n = 9600$ g·mol⁻¹ (according to GPC measurements) were synthesized and cross-linked by polyaddition reaction using an aliphatic diisocyanate as described in.^[13]

Characterization Techniques

The GPC measurements, DSC measurements, and tensile tests were performed as

stated in.^[20] For investigations in cyclic thermomechanical measurements polymer films were cut into standard samples (ISO 527-2/1BB) and strained at an elongation rate of $10 \text{ mm} \cdot \text{min}^{-1}$. TSCP and recovery experiments were conducted in cyclic, thermomechanical measurements. In TSCP1 the sample was stretched $\varepsilon_B^0 = 50\%$ at T_{high} (100°C), equilibrated for 5 min, cooled with a cooling rate of $5 \text{ K} \cdot \text{min}^{-1}$ to T_{mid} (60°C) under stress-controlled conditions and unloaded after 120 min equilibration time resulting in shape (B) being represented by ε_B . The sample was then further stretched to the maximum programmed elongation of $\varepsilon_A^0 = 100\%$ and cooled to T_{low} (0°C) under stress-control with a cooling rate of $5 \text{ K} \cdot \text{min}^{-1}$. After 10 min the sample was unloaded leading to shape (A) being represented by ε_A . In TSCP2 the sample was cooled with $5 \text{ K} \cdot \text{min}^{-1}$ to T_{low} (0°C) under stress-control after the first stretching to 50% and unloaded after 10 min equilibrating at T_{low} . The sample was then heated to T_{mid} (60°C) with $2 \text{ K} \cdot \text{min}^{-1}$ 10 min equilibrated while assuming shape (B) (represented by ε_B) and was then further programmed according to TSCP. The recovery process of the samples was monitored by reheating with a heating rate of $1 \text{ K} \cdot \text{min}^{-1}$ from T_{low} to T_{high} while the stress was kept at 0 MPa. The two steps of the shape recovery were separated by a minimum of the recovery rate at the inflection point of the recovery curve being represented by ε_{ip} , while the recovered shape (C) is represented by ε_C . The T_{sws} , which represent the temperatures at the maximum shape recovery rates were determined at maximal absolute values of $\Delta\varepsilon/\Delta T$ during the recovery process. The strain recovery ratios R_r were determined using the following equations (N is the cycle number):

$$R_r(A \rightarrow B) = \frac{\varepsilon_A(N) - \varepsilon_{\text{ip}}(N)}{\varepsilon_A(N) - \varepsilon_B(N)} \quad (1)$$

$$R_r(A \rightarrow C) = \frac{\varepsilon_A(N) - \varepsilon_C(N)}{\varepsilon_A(N) - \varepsilon_C(N-1)} \quad (2)$$

All cyclic thermo-mechanical measurements were conducted five times. The ratio of a single recovery step relative to the overall recovery $\Delta\varepsilon_{\text{rel}}(A \rightarrow B)$ and $\Delta\varepsilon_{\text{rel}}(B \rightarrow C)$ in all recovery experiments were calculated according to Equation (3 and 4):

$$\Delta\varepsilon_{\text{rel}}(A \rightarrow B) = \frac{\varepsilon_A - \varepsilon_{\text{ip}}}{\varepsilon_A - \varepsilon_C} \quad (3)$$

$$\Delta\varepsilon_{\text{rel}}(A \rightarrow C) = \frac{\varepsilon_{\text{ip}} - \varepsilon_C}{\varepsilon_A - \varepsilon_C} \quad (4)$$

The temperature interval between 10 and 90% of shape recovery (ΔT_{rec}) was used as a measure for the distinctiveness of the recovery steps, calculated according to Equations (5) and (6), whereas ε_{10} and ε_{90} denote the elongations at 10% respectively 90% shape recovery of the related recovery step:

$$\Delta T_{\text{rec}}(A \rightarrow B) = T(\varepsilon_{90(A \rightarrow B)}) - T(\varepsilon_{10(A \rightarrow B)}) \quad (5)$$

$$\Delta T_{\text{rec}}(B \rightarrow C) = T(\varepsilon_{90(B \rightarrow C)}) - T(\varepsilon_{10(B \rightarrow C)}) \quad (6)$$

Results and Discussion

All five synthesized copolymer networks exhibited gel content values between 92 and 98% indicating an almost complete crosslinking reaction. Thermal characterization was performed by DSC measurements and resulted in two sufficiently separated ($\Delta T > 20 \text{ K}$) T_{mS} and T_{cS} associated to the two switching segments. The only exception was the copolymer network having $\mu_{\text{PCL}} = 75 \text{ wt\%}$ showing a third T_c close to $T_{\text{c,PCL}}$ but being related to the PPD segment. The PCL melting point ($T_{\text{m,PCL}}$) was found between 35 and 43°C , while the PPD related $T_{\text{m,PPD}}$ varied between 70 and 79°C .^[13]

In order to obtain TSC, the influences of the segments on each other in the crystallization process during the programming procedure have to be limited, which was achieved so far by adjustment of the

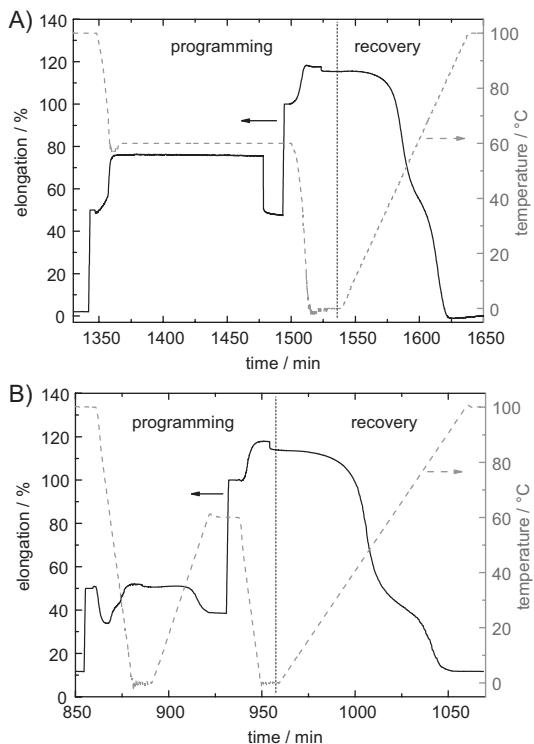


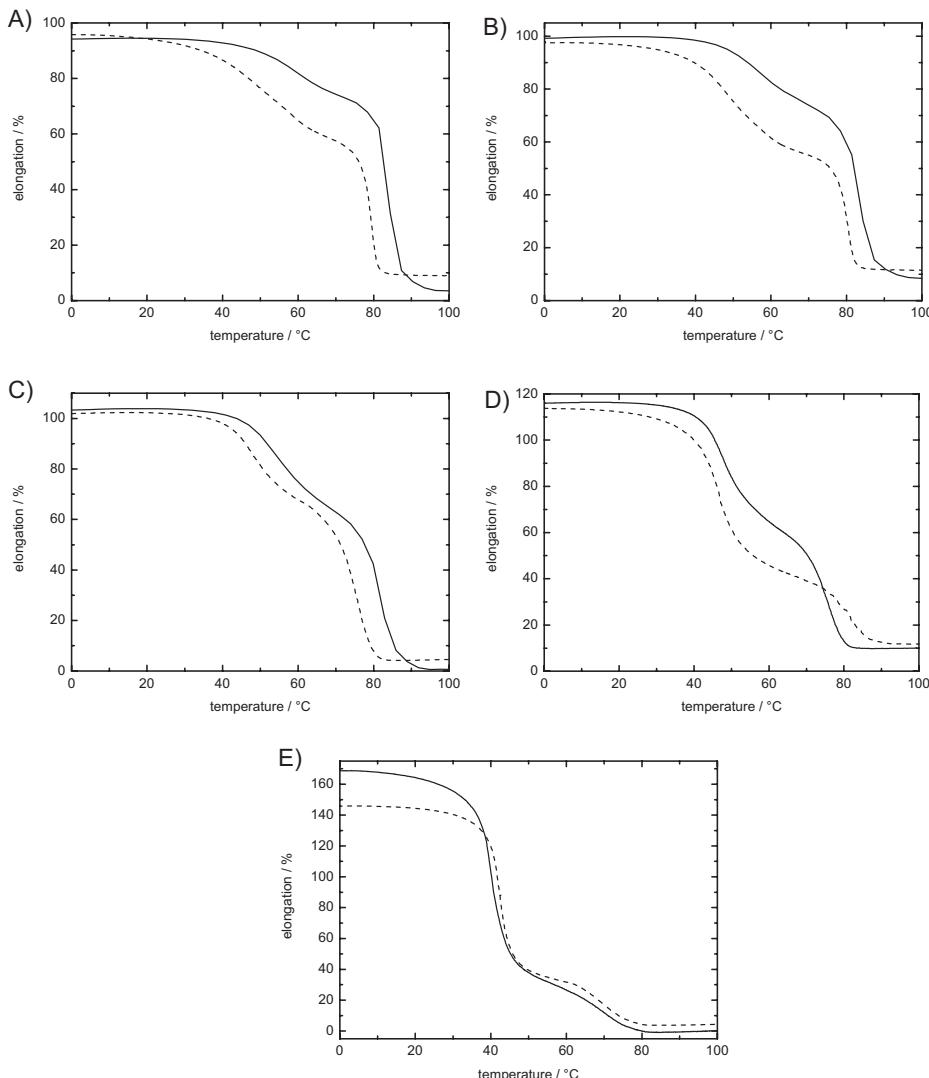
Figure 1.

Comparison of two TSCP, 5th cycle of triple-shape experiments; A: In TSCP1 samples were stretched to 50% elongation at T_{high} , cooled to T_{mid} and unloaded after 2 hours equilibration time. The sample was then further programmed to 100% elongation, cooled to T_{low} under stress-control, and unloaded after 10 min equilibration time. B: In TSCP2 samples were stretched to 50% elongation at T_{high} , cooled to T_{low} under stress-control and unloaded after 10 min equilibration time. The sample was then heated to T_{mid} , further programmed to 100% elongation, and again cooled to T_{low} under stress-control before unloading after 10 min equilibration.

copolymer composition. After application of TSCP1 TSC could be obtained from copolymer networks based on PPD precursors with $M_n = 5100 \text{ g} \cdot \text{mol}^{-1}$, PCL precursors with $M_n > 5000 \text{ g} \cdot \text{mol}^{-1}$ and a PCL content $\mu_{\text{PCL}} > 25 \text{ wt\%}$ in the network synthesis. A clear triple-shape effect was obtained for the materials with $\mu_{\text{PCL}} = 50$ or 60 wt%.^[13] Values of μ_{PCL} of 25, 40 or 75 wt% were considered to be unfavorable since triple-shape characteristics deteriorated: ΔT_{rec} of a recovery step was increasing with decreasing content of the related segment in the copolymer network. Also, the $\Delta \varepsilon_{\text{rel}}$ values were shifting with increasing difference to the 50%:50% ratio in which the programming steps were performed. All these differences could be

explained by the crystallization behavior of the copolymer networks, especially by the tendency of the PPD segments to crystallize from a mixed amorphous phase at lower temperatures with the T_c close to the T_c of the PCL phase and thus negatively affecting the shape fixation during the first programming step.

Applying TSCP2, the crystallization of the segments could be influenced by variations of the sequence of programming temperatures leading to enhanced triple-shape characteristics of the copolymer networks. In TSCP2 the first cooling step after the first deformation of the sample was carried out until T_{low} (0 °C) was reached. That ensured a completed crystallization of the crystallizable PPD domains.

**Figure 2.**

Recovery curves, elongation as function of the temperature; solid line: after TSCP; dashed line: after TCSP2. A: $^3\text{PPD}^4\text{PCL}(25)$; B: $^3\text{PPD}^4\text{PCL}(40)$; C: $^3\text{PPD}^4\text{PCL}(50)$; D: $^3\text{PPD}^4\text{PCL}(60)$; E: $^3\text{PPD}^4\text{PCL}(75)$.

The subsequent heating step to T_{mid} resulted in the melting of the crystallized PCL domains, which then could be deformed during the second programming step (see Figure 1). In this way the fixation of the two temporary shapes was limited to only one switching segment respectively.

The recovery curves as function of the temperature are shown in Figure 2, the values of the triple-shape characteristics are summarized in Table 1. The recovery

steps were characterized by the temperature interval between the two temperatures determining 10 and 90% recovery (ΔT_{rec}) of the related recovery step. It can be seen that ΔT_{rec} for the second shape-recovery step related to the PPD switching segment after TSCP2 with values between 7 and 14 K was up to 5 K smaller as after application of TSCP1 reaching values between 9 and 15 K. Hence, as a result of TSCP2 the first programmed deformation could be fixed

Table 1.

Triple-shape effect of copolymer networks. Values are average values over cycles 2–5 (1–5 for temperatures) \pm standard deviation.

Sample ID ^{a)}	R _r		$\Delta\varepsilon_{\text{rel}}$		T _{sw1}	T _{sw2}	ΔT_{rec} (A \rightarrow B)	ΔT_{rec} (B \rightarrow C)
	(A \rightarrow B)	(A \rightarrow C)	(A \rightarrow B)	(B \rightarrow C)				
	[%]	[%]	[%]	[%]	[°C]	[°C]	[K]	[K]
TSCP1	³ PPD ⁴ PCL(25)	78.6 \pm 2.5	99.9 \pm 2.5	24 \pm 3	76 \pm 3	59 \pm 2	84 \pm 1	26 \pm 3
	³ PPD ⁴ PCL(40)	86.2 \pm 5.5	99.9 \pm 4.0	28 \pm 3	72 \pm 3	57 \pm 2	84 \pm 1	20 \pm 3
	³ PPD ⁴ PCL(50)	84.0 \pm 0.7	99.9 \pm 0.5	36 \pm 1	64 \pm 1	55 \pm 2	82 \pm 1	20 \pm 1
	³ PPD ⁴ PCL(60)	88.2 \pm 0.9	99.9 \pm 0.7	51 \pm 2	49 \pm 2	48 \pm 1	76 \pm 1	20 \pm 1
	³ PPD ⁴ PCL(75)	86.3 \pm 0.5	99.9 \pm 0.5	83 \pm 1	17 \pm 1	40 \pm 1	70 \pm 1	17 \pm 1
TSCP2	³ PPD ⁴ PCL(25)	79.3 \pm 0.4	99.1 \pm 0.5	42 \pm 3	58 \pm 3	57 \pm 1	79 \pm 1	33 \pm 1
	³ PPD ⁴ PCL(40)	86.4 \pm 1.0	99.0 \pm 0.9	45 \pm 3	55 \pm 3	49 \pm 1	80 \pm 1	27 \pm 1
	³ PPD ⁴ PCL(50)	92.9 \pm 0.8	99.8 \pm 0.1	36 \pm 1	64 \pm 1	48 \pm 1	75 \pm 1	18 \pm 1
	³ PPD ⁴ PCL(60)	96.8 \pm 1.5	98.9 \pm 0.7	67 \pm 6	33 \pm 6	47 \pm 2	81 \pm 2	22 \pm 2
	³ PPD ⁴ PCL(75)	97.7 \pm 0.2	99.9 \pm 0.4	80 \pm 1	20 \pm 1	42 \pm 1	70 \pm 2	12 \pm 1

^{a)}³PPD⁴PCL(x) are copolymer networks from ³PPD segments and ⁴PCL segments with μ_{PCL} (x wt%) given in parenthesis.

by PPD crystallites exhibiting a smaller melting range.

In TSCP1 and TSCP2 both temporary shapes were programmed by a deformation of 50% each (50% in the first step and a total of 100% in the second step). Therefore, assuming sufficient shape fixation by the related switching segment, a nearly equal shape recovery was expected, being characterized by the ratio of the shape recovery relative to the overall recovery ($\Delta\varepsilon_{\text{rel}}$). This can be illustrated by the difference in the $\Delta\varepsilon_{\text{rel}}$ values of both recovery steps $D(\Delta\varepsilon_{\text{rel}})$, which should be close to zero. However, after application of TSCP1 relative recovery ratios near 50% were only obtained in copolymer networks with $\mu_{\text{PCL}} = 50$ or 60 wt%. After applica-

tion of TSCP2, the relative recovery ratios of both recovery steps were closer to the expected 50:50 recovery in all investigated copolymer networks except for $\mu_{\text{PCL}} = 60$ wt%. This result is also attributed to a better shape fixation by the respective switching segment.

After TSCP1 the switching temperatures showed a strong dependence from the copolymer composition by decreasing with increasing PCL content. After TSCP2 this effect was significantly diminished, which could be attributed to the separated crystallization processes of the switching segments. However, after TSCP2 in copolymer networks with $\mu_{\text{PCL}} < 60$ wt% the switching temperatures were reduced.

Table 2.

Positive (“+”) and negative (“−”) influence of TSCP2 on triple-shape properties (compared to TSCP1), “o” no influence.

copolymer networks					
μ_{PCL} [wt%]	25	40	50	60	75
$R_r(A \rightarrow B)$ ^{a)}	o	o	+	+	+
$R_r(A \rightarrow C)$ ^{a)}	o	o	o	o	o
$D(\Delta\varepsilon_{\text{rel}})$ ^{b)}	+	+	o	−	+
$\Delta T_{\text{rec}}(A \rightarrow B)$ ^{c)}	−	−	+	−	+
$\Delta T_{\text{rec}}(B \rightarrow C)$ ^{c)}	+	+	o	o	+

^{a)}A change in R_r values is only indicated if the difference is more than 1%; ^{b)}a decrease of the difference D is beneficial; ^{c)}a decrease of the ΔT_{rec} values is beneficial.

Conclusion

The application of the modified TSCP2 enabled to a certain extent a better control of the TSE in copolymer networks based on star-shaped PPD and PCL precursors by influencing the crystallization behavior of the two switching segments.

Compared to the TSE after application of TSCP1, the shape fixation by the respective switching segment was significantly enhanced by TSCP2. The temperature interval of $T_{\text{rec}}(B \rightarrow C)$ was reduced for three compositions of the copolymer net-

work. Furthermore, the relative ratios of the shape recovery for both recovery steps were closer to the programmed ratio. The change in the values characterizing the triple-shape properties of all five copolymer networks is summarized in Table 2.

- [1] M. Behl, J. Zottmann, A. Lendlein, *Adv. Polym. Sci.* **2010**, 226, 1.
- [2] K. Gall, M. L. Dunn, Y. P. Liu, D. Finch, M. Lake, N. A. Munshi, *Acta Mater.* **2002**, 50, 5115.
- [3] I. S. Kolesov, K. Kratz, A. Lendlein, H.-J. Radusch, *Polymer* **2009**, 50, 5490.
- [4] Y. J. Liu, H. B. Lv, X. Lan, J. S. Leng, S. Y. Du, *Compos. Sci. Technol.* **2009**, 69, 2064.
- [5] X. F. Luo, P. T. Mather, *Adv. Funct. Mater.* **2010**, 20, 2649.
- [6] S. Mondal, *Mini-Rev. Org. Chem.* **2009**, 6, 114.
- [7] D. Ratna, J. Karger-Kocsis, *J. Mater. Sci.* **2008**, 43, 254.
- [8] M. Behl, M. Y. Razzaq, A. Lendlein, *Adv. Mater.* **2010**, 22, 3388.
- [9] A. Kulkarni, J. Reiche, J. Hartmann, K. Kratz, A. Lendlein, *Eur. J. Pharm. Biopharm.* **2008**, 68, 46.
- [10] R. Langer, D. A. Tirrell, *Nature* **2004**, 428, 487.
- [11] A. T. Neffe, B. D. Hanh, S. Steuer, A. Lendlein, *Adv. Mater.* **2009**, 21, 3394.
- [12] M. Behl, I. Bellin, S. Kelch, W. Wagermaier, A. Lendlein, *Adv. Funct. Mater.* **2009**, 19, 102.
- [13] J. Zottmann, M. Behl, Y. Feng, A. Lendlein, *Adv. Funct. Mater.* **2010**, 20, 3583.
- [14] M. Behl, A. Lendlein, *J. Mater. Chem.* **2010**, 20, 3335.
- [15] I. Bellin, S. Kelch, R. Langer, A. Lendlein, *Proc. Natl. Acad. Sci. USA* **2006**, 103, 18043.
- [16] I. Bellin, S. Kelch, A. Lendlein, *J. Mater. Chem.* **2007**, 17, 2885.
- [17] J.-J. Li, T. Xie, *Macromolecules* **2011**, 44, 175.
- [18] T. Pretsch, *Polym. Degrad. Stab.* **2010**, 95, 2515.
- [19] U. N. Kumar, K. Kratz, W. Wagermaier, M. Behl, A. Lendlein, *J. Mater. Chem.* **2010**, 20, 3404.
- [20] J. Zottmann, M. Behl, D. Hofmann, A. Lendlein, *Adv. Mater.* **2010**, 22, 3424.