Quadruple-shape hydrogels

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Abstract
The capability of directed movements by two subsequent shape changes could be implemented in shape-memory hydrogels by incorporation of two types of crystallizable side chains. While in non-swollen polymer networks even more directed movements could be realized, the creation of multi-shape hydrogels is still a challenge. We hypothesize that a quadruple-shape effect in hydrogels can be realized, when a swelling capacity almost independent of temperature is generated, whereby directed movements could be enabled, which are not related to swelling. In this case, entropy elastic recovery could be realized by hydrophilic segments and the fixation of different macroscopic shapes by means of three semi-crystalline side chains generating temporary crosslinks. Monomethacrylated semi-crystalline oligomers were connected as side chains in a hydrophilic polymer network via radical copolymerization. Computer assisted modelling was utilized to design a demonstrator capable of complex shape shifts by creating a casting mold via 3D printing from polyvinyl alcohol. The demonstrator was obtained after copolymerization of polymer network forming components within the mold, which was subsequently dissolved in water. A thermally-induced quadruple-shape effect was realized after equilibrium swelling of the polymer network in water. Three directed movements were successfully obtained when the temperature was continuously increased from 5°C to 90°C with a recovery ratio of the original shape above 90%. Hence, a thermally-induced quadruple-shape effect as new record for hydrogels was realized. Here, the temperature range for the multi-shape effect was limited by water as swelling media (0°C–100°C), simultaneously distinctly separated thermal transitions were required, and the overall elasticity indispensable for successive deformations was reduced as result of partially chain segment orientation induced by swelling in water. Conclusively the challenges for penta- or hexa-shape gels are the design of systems enabling higher elastic deformability and covering a larger temperature range by switching to a different solvent.

Keywords: shape-memory, hydrogels, semi-crystalline

(Some figures may appear in colour only in the online journal)

1. Introduction
The capability of a polymeric material to adjust its characteristics as function of environmental modifications is exciting in order to explore fundamental principles and to enable challenging applications \cite{1–3}. Here, especially soft stimuli-sensitive materials like shape-memory hydrogels (SMHs) providing on demand changes in mechanical properties and macroscopic shape are fascinating candidate materials for the design of fasteners, anchoring systems or release devices in aqueous environments \cite{4}. In contrast to hydrogels capable of volume changes based on sol-gel transitions \cite{5}, SMHs can switch between formerly programmed shapes by directed movements \cite{6}. Here, switching segments generating reversible temporary crosslinks are required, which enable the fixation of a deformed temporary shape. The deformation decreases the entropy of the polymeric network, which is kinetically frozen by the formation of temporary crosslinks. Once, temporary crosslinks are released when an external stimulus is applied, a directed movement driven by entropy elasticity to the original permanent shape is obtained. Here, the covalent netpoints prevent the complete dissolution.
of the hydrogel matrix. Switching segments able to generate these temporary crosslinks in a water-rich environment based on short crystallizable side chains [7], oligomeric crystallizable side chains [8], moieties for host-guest interactions [9], and for complex formation [10] were reported. In case of non-swollen polymeric networks, complex macroscopic movements were realized with materials providing a triple-, quadruple-, and even a quintuple-shape behavior. Here, semi-crystalline polymeric networks [11], particularly thermo-sensitive polyurethanes [12], semi-interpenetrating polymer networks [13], and ternary polymeric composites [14] providing a broad glass transition temperature ($T_g$) or separated thermal transitions composed of $T_g$s and melting temperatures ($T_m$s) did qualify for the design of these multiple-shape materials. This competition to increase the potential number of shape shifts is challenging when hydrogels act as functional material basis. Caused by the high water content in hydrogels, a lower effectivity for the directed movements was assumed in vitrifiable materials as the high number of water molecules could result in plasticization and hydration [15]. Accordingly, fixation by crystallization was a preferred design when reversible fixation was required. Complex directed movements of hydrogels were reported for example for triple-shape hydrogels, which enabled two steps of shape switching. The introduction of two types of hydrophobic side chains as switching segments in a hydrogel matrix provided the generation of two distinct crystalline domains exhibiting different $T_m$s [16]. The directed movements were realized by heat as stimulus by increasing the temperature first above the lower melting transition and second by an increase in temperature also above the higher melting transition. Another concept to design hydrogels with a triple-shape effect concentrated on the formation of dipole–dipole interactions as one type of temporary crosslinks and complexes with zinc-ions as second type [15]. These temporary crosslinks could be dissociated by the addition of a solution of a high zinc concentration resulting in this way in the directed movement to two different shapes. Complex movements in SMHs were furthermore realized by host-guest interactions and the formation of aggregates acting as physical crosslinks [17]. In this case, changes in the wavelength of light or pH values induced the directed movements. When a precise sequence (1. Ca$^{2+}$-ions, 2. H$_2$O$_2$, and 3. heat) was kept, even complex movements with more than three changes in shape could be realized [18].

In this work we explored, whether a quadruple-shape effect as a new record for stimuli-sensitive hydrogels can be solely heat induced. In this case, hydrogels could be designed based on temperature-sensitive switching segments, e.g., semi-crystalline oligomers. Here, the challenge is the creation of a water swollen polymeric material, in which the interactions between the different phases (three crystallizable switching segments) and between switching segments and the swelling segment are suppressed. Consequently, co-crystallization processes (resulting in changed thermal properties) could be avoided and a swelling behavior independent of changes in temperature (as required for the formation and release of temporary crosslinks for a thermally-induced SMHs) could be achieved. Our approach to address these challenges bases on three different types (based on different repeating units) of hydrophobic, semi-crystalline oligomers, which could act as switching segments providing temporary crosslinks. These switching segments should be incorporated in hydrophilic polymer networks based on N-vinylpyrrolidone (NVP) as backbone forming swelling segment and oligo(ethylene glycol) dimethacrylate as crosslinker (grey), and the side chains OPDL (red), OCL (green), and OTHF (yellow) acting as switching segments. (Scheme 1(A)). In order to realize the potentially four different shapes, the domains associated to the different types of switching segments need to provide distinct thermal melting transitions. Here, oligo-tetraydrofuran (OTHF), oligo (ε-caprolactone) (OCL), and oligo (ω-pentadecalactone) (OPDL) were selected, as these hydrophobic oligomers provide $T_m$s which can be adapted to different temperature intervals ($T_m < 30°C$ for OTHF, $40°C < T_m < 60°C$ for OCL, $T_m > 70°C$ for OPDL). In order to avoid swelling effects, which could interfere with the directed movements, the switching segments should be integrated into the hydrophilic polymer network as side chains, whereby the influence of thermal transitions on the mesh size of the network structure could be suppressed as phase separation phenomena could be facilitated. The designed
hydrogels were characterized in terms of the swelling capacity, thermal and thermo-mechanical properties, as well as the ability of a quadruple-shape effect. The applied programming and the obtained recovery process are schematically illustrated in scheme 1(B). Here, the permanent shape A can be converted to the first temporary shape B after deformation at 90°C and fixation at 60°C, whereby the new macroscopic shape is stabilized once crystalline OPDL domains are formed. The deformation at 60°C and the subsequent formation of temporary crosslinks by OCL crystallization (at 30°C) fixes the second temporary shape C. The third macroscopic shape, denominated as shape D can be obtained when the hydrogel is deformed once again and can be fixed by reducing the temperature to 5°C resulting in crystallization of OTHF side chains. The stepwise increase in temperature from 5°C over 30°C and 60°C–90°C would initiate the recovery process resulting in three directed movements from shape D to shape C, from shape C to shape B, and finally from shape B to the original shape A.

2. Materials and methods

2.1. Materials

Chemicals were obtained from Sigma-Aldrich (Tauk kirchen, Germany) and were used as received if not otherwise mentioned. The ε-caprolactone (CL) and ω-pentadecalactone were purified by distillation over potassium hydroxide (Merck, Darmstadt, Germany). Azobisisobutyronitril (AIBN) was recrystallized from ethanol. Inhibitor in oligo(ethylene glycol dimethacrylate) (OEGDMA, Polysciences, Inc.) was removed by passing through a column filled with inhibitor removal (MEHQ remover). 1, 4-Dioxane was distilled prior to usage. THF was dried under argon atmosphere with sodium at 70°C in the presence of benzenophene and was distilled.

2.2. Synthesis of quadruple-shape hydrogels

2.2.1. Synthesis of oligomers. Synthesis of OCL-OH according to [16]: under an argon atmosphere 137 mmol CL were molten at 130°C in a Schlenk flask, 4 mmol 1-hexanol and 0.2 mmol dibutyltin oxide (DBTO) were added, and the reaction mixture was stirred at 130°C for 7 h. Afterwards the reaction product was dissolved in dichloromethane (DCM), precipitated from cold hexane, filtered off, washed with cold hexane, and dried under vacuum until constant weight was achieved.

1H-NMR (500 MHz, CDCl3): δ [ppm] = 4.06 (t, COO–CH2); 3.65 (t, CH2–OH); 2.30 (t, CH2–COO); 1.65 (m, COO–CH2–CH2–H2–CH2–COO, and CH2–CH2–OH); 1.38 (m, CH3–CH2–CH2–H2, COO–CH2–CH2–CH2, and CH2–CH2–CH2–OH); 0.89 (t, CH3).

Synthesis of OTHF-OH according to [19]: in a Schlenk flask 10 ml DCM, 18 mmol tetramethylpiperidine (TMP), and 18 mmol triflic anhydride were added at 0°C under an argon atmosphere. After 5 min under intensive stirring of the mixture, 18 mmol 1-hexanol were added. The reaction mixture was stirred at 0°C for 1 h. Afterwards the reaction mixture was heated to 25°C and under intensive stirring 500 ml THF was added. After 45 min, 1.5 ml distilled water was added to stop the reaction. The solvents were removed in vacuum, the oligomer was dissolved in ethyl acetate, extracted with water, NH4Cl-solution, and NaCl-sat.-solution until pH = 7 was achieved and then dried under vacuum. Afterwards THF was added, and the oligomer was precipitated from cold hexane, filtered off, and dried under vacuum until constant weight was achieved.

1H-NMR (500 MHz, CDCl3): δ [ppm] = 3.40 (m CH2–O); 1.61 (m, CH2–CH2–O); 1.46 (m, CH2–CH3); 1.29 (m, CH3–CH2–CH2–CH3); 0.88 (t, CH3).

Synthesis of OPDL-OH according to [8]: In a Schlenk flask 109 mmol ω-pentadecalactone were molten at 130°C under argon atmosphere, and under intensive stirring 11 mmol 1-hexanol and 0.08 mmol of dibutyltin oxide were added. The reaction mixture was stirred at 130°C for 6 d. Afterwards the product was dissolved in chloroform, precipitated from hexane, filtered off, and dried under vacuum until constant weight was achieved.

1H-NMR (500 MHz, CDCl3): δ [ppm] = 4.00 (t, COO–CH2); 3.65 (t, CH2–OH); 2.28 (t, CH2–COO); 1.61 (m, COO–CH2–CH2); 1.25 (m, CH2–CH2–CH2–CH2–COO, COO–CH2–CH2–(CH2)3–CH3); 0.89 (t, CH3).

2.2.2. End group functionalization of oligomers. In a Schlenk flask 5.5 mmol oligomer (OCL-OH, PDPL-OH, or OTHF-OH) were dissolved at room temperature under argon atmosphere in 120 ml DCM. 7 mmol 2-isocyanatoethyl methacrylate (IEMA) and 0.02 mmol of dibutyltin dilaurate (DBTL) were added under intensive stirring. After 5 d the IEMA functionalized product was precipitated from hexane/diethyl ether/methanol (18/1/1 vol%), filtered off, and dried under vacuum until constant weight was achieved.

2.2.3. Synthesis of hydrogels. Polymer networks were prepared according to [16] by mixing OCL-IEMA, PDPL-IEMA, OTHF-IEMA, NVP, OEGDMA (0.5 mol% relative to vinyl and methacrylate groups), and AIBN (1.5 mol% related to all vinyl and methacrylate groups) with a concentration of 70 wt% reactants in 1, 4-dioxane at 60°C. The mixture was poured between glass plates (10 cm × 10 cm) equipped with a 2 mm Teflon® spacer, which were kept at 75°C for 24 h. The obtained polymer networks were extracted with 1, 4-dioxane and finally swollen in distilled water to equilibrium.

2.3. Characterization methods

2.3.1. GPC. Number average of molecular weights (Mn) of the precursors were determined for two times on a multidetector GPC consisting of a precolumn, two 300 × 0.8 mm M columns (Polymer Standards Service GmbH, Mainz, Germany), an isocratic pump 2080, an automatic injector AS 2050 (both Jasco, Tokyo, Japan), a RI detector Shodex RI-101 (Showa Denko, Munchen, Germany), and a dual detector T60A (Viscotek Corporation, Houston, USA)
using chloroform (0.2 wt% toluene as internal standard, 35 °C, 1.0 ml min⁻¹) as eluent.

2.3.2. NMR. ¹H-NMR spectra were recorded at 25 °C in DMSO-d₆ with a Bruker Avance 500 spectrometer (500 MHz, Bruker, Karlsruhe, Germany) with a relaxation time of 2 s.

2.3.3. Gel content and swelling in water. The gel content \( G_c \) was calculated as the ratio of the non-swollen \( m_0 \), and the extracted mass \( m_{ex} \) determined from swelling experiments at 25 °C according to the following equation. Chloroform was used as swelling agent.

\[
G_c = \frac{m_{ex}}{m_0} \cdot 100\%.
\]

The volumetric degree of swelling \( Q \) was determined at different temperatures in water after 24 h of swelling and was calculated according to the equation:

\[
Q = 1 + \rho_2 \cdot \left( \frac{m_{sw}}{m_{ex} \cdot \rho_1} - 1 \right).
\]

The mass of the sample in the swollen state is described by \( m_{sw} \), \( \rho_1 \) represents the density of the swelling medium (e.g. water), and \( \rho_2 \) is the density of the dry polymer network. The density \( \rho_2 \) was determined with an Ultra Pycnometer (Quantachrome, Odelzhausen, Germany) at 25 °C using a measurement cell with a calibration volume of 1.0725 cm³.

2.3.4. Light microscopy. The morphology of hydrogels was investigated by light microscopy (Axio Imager.A1m, Carl Zeiss Microimaging, Göttingen, Germany) on glass slides. 20 μm slices were prepared with a microtome of samples in the swelling equilibrium in water. Samples were analyzed in the swollen state in water.

2.3.5. DSC. Differential scanning calorimetry (DSC) experiments were performed on a Netzsch DSC 204 Phoenix (Netzsch, Selb, Germany) in the temperature range between 0 °C and 100 °C with heating and cooling rates of 10 K min⁻¹ in sealed aluminum pans. Thermal properties were determined from the second heating run. Oligomers were measured in dry state, while hydrogels were investigated in the equilibrium swollen state.

2.3.6. Rheology. Thermo-mechanical properties were investigated by shear oscillation measurements on a Haake Rheowin Mars II (Thermo Scientific, Karlsruhe, Germany) using a plate-plate geometry. Measurements were carried out in a temperature range between 10 °C and 95 °C with heating rates of 10 K min⁻¹. Oscillation measurements were performed with a constant amplitude of 4 Pa, a constant frequency of 1 Hz, and with distilled water.

2.3.7. Quantification of Quadruple-shape effect. Quadruple-shape experiments were performed using standard test specimen (ISO 527-2/1BB) on a Zwick 2.5 (Zwick, Ulm, Germany), equipped with a 20 N load cell at a deformation rate of 10 mm min⁻¹. The tensile clamps (screw clamps) were submerged in a 101 distilled water tank, whose temperature was controlled by a Lauda ECO (Lauda, Lauda-Königshofen, Germany). The cyclic thermomechanical tests consisted of six cycles, in which the first one was the preconditioning cycle. Each cycle consisted of a programming and a recovery module.

During the programming process the sample was heated to 90 °C, equilibrated for 3 min, deformed to a programming strain for shape B \( \varepsilon_{B, \text{load}} \) (typically 50%) and cooled to 60 °C under constant strain. Afterwards the stress was released resulting in \( \varepsilon_B \). Then the sample was deformed to a programming strain for shape C \( \varepsilon_{C, \text{load}} \) (typically 75%) and cooled to 30 °C under constant strain. After releasing the stress, \( \varepsilon_C \) is obtained. Subsequently, the specimen was deformed to a programming strain for shape D \( \varepsilon_{D, \text{load}} \) (typically 100%) and cooled to 5 °C under constant strain. \( \varepsilon_D \) can be achieved when the stress is released. The recovery process of the different temporary shapes and the permanent shape was performed under stress free conditions. Here, the temperature was increased from 5 °C to 30 °C resulting in the temporary shape C with \( \varepsilon_{C, \text{rec}} \). Subsequently, the specimen was furthermore increased to 60 °C, whereby shape B was recovered with \( \varepsilon_{B, \text{rec}} \). The original shape A with \( \varepsilon_{A, \text{rec}} \) was obtained when the temperature was increased to 90 °C. The shape-memory properties were determined for each individual shape, i.e. shape A–B, B–C, and C–D. For each transition, the shape fixity ratio \( R_f \) and the shape recovery ratio \( R_c \) were calculated according to subsequent equations where \( \varepsilon_x \) describes the elongation of the previous shape (during programming process; e.g. the elongation of shape A when shape B was obtained) or of the recovered shape (during the recovery process) and \( \varepsilon_x \) describes the elongation of the fixed shape (in the programming cycle) or of the previous shape (during recovery process; e.g. the elongation of shape B when shape A was recovered):

\[
R_f (x - y) = \frac{\varepsilon_y - \varepsilon_x}{\varepsilon_y - \varepsilon_{x, \text{rec}}} \quad R_c (y - x) = \frac{\varepsilon_y - \varepsilon_{x, \text{rec}}}{\varepsilon_y - \varepsilon_x}.
\]

3. Results and discussion

3.1. Synthesis and swelling behavior of Quadruple-shape hydrogels

The hydrophobic switching segments, which are required to generate reversible temporary crosslinks by crystallization should be implemented into the hydrogel network as side chains. In this way, a swelling behavior in water which would be independent of the state of the switching segments
might be suitable for the generation of distinct separated and difference of at least 20 different state. Hence, monofunctionalized oligomers (OTHF-OH, OCL-OH, and OPDL-OH) were prepared by ring-opening polymerization of the corresponding monomers tetrahydrofuran, ε-caprolactone, and ω-pentadecalactone using 1-hexanol as initiator. Separated melting transitions within the range of 0 and 100 °C (according to the temperature range of water in a liquid state) were required for the creation of quadruple-shape droplets, resulting in the following design criteria for the different $T_m$: $20^\circ C < T_{m,1} < 30^\circ C$; $40^\circ C < T_{m,2} < 60^\circ C$, and $70^\circ C < T_{m,3} < 90^\circ C$. Hence, the oligomer chain lengths of OTHF, OCL, and OPDL had to be adapted according to the dependencies between molecular weight and thermal properties. Here, oligotetrahydrofuran (OTHF), oligo(ε-caprolactone) (OCL), and oligo(ω-pentadecalactone) (OPDL) were selected, as these hydrophobic oligomers provide $T_m$s which can be adapted to different temperature intervals. Hence, the molecular weight of OTHF-OH was calculated to 4000 g mol$^{-1}$ (capability to crystallize with a melting transition about 25 °C), of OCL-OH to 2000 g mol$^{-1}$ (distinct different thermal properties in comparison to OTHF-OH with $T_m$ ~ 50 °C), and of OPDL-OH to 2500 g mol$^{-1}$ ($T_m$ ~ 85 °C) as the boiling point of water presents the upper limit for the programming and recovery process.

![Figure 1](https://example.com/figure1.jpg)

**Figure 1.** Light microscopy image of a quadruple-shape hydrogel containing 40 wt% OTHF, 20 wt% OCL, and 10 wt% OPDL in the swelling equilibrium in water. Left: Bright-field light microscopy, right: polarized light microscopy.

(semi-crystalline or amorphous) could be realized. Here, the created hydrophobic domains would not influence the polymer main chain as swelling segments and might act as oil in water droplets, which are not able to uptake water in an amorphous state. Hence, monofunctionalized oligomers (OTHF-OH, OCL-OH, and OPDL-OH) were prepared by ring-opening polymerization of the corresponding monomers tetrahydrofuran, ε-caprolactone, and ω-pentadecalactone using 1-hexanol as initiator. Separated melting transitions within the range of 0 and 100 °C (according to the temperature range of water in a liquid state) were required for the creation of quadruple-shape droplets, resulting in the following design criteria for the different $T_m$: $20^\circ C < T_{m,1} < 30^\circ C$; $40^\circ C < T_{m,2} < 60^\circ C$, and $70^\circ C < T_{m,3} < 90^\circ C$. Hence, the oligomer chain lengths of OTHF, OCL, and OPDL had to be adapted according to the dependencies between molecular weight and thermal properties. Here, oligotetrahydrofuran (OTHF), oligo(ε-caprolactone) (OCL), and oligo(ω-pentadecalactone) (OPDL) were selected, as these hydrophobic oligomers provide $T_m$s which can be adapted to different temperature intervals. Hence, the molecular weight of OTHF-OH was calculated to 4000 g mol$^{-1}$ (capability to crystallize with a melting transition about 25 °C), of OCL-OH to 2000 g mol$^{-1}$ (distinct different thermal properties in comparison to OTHF-OH with $T_m$ ~ 50 °C), and of OPDL-OH to 2500 g mol$^{-1}$ ($T_m$ ~ 85 °C) as the boiling point of water presents the upper limit for the programming and recovery process.

The obtained hydroxy end groups were subsequently converted with 2-isocyanatoethyl methacrylate (IEMA) to obtain the methacrylated oligomers OTHF-IEMA, OCL-IEMA, and OPDL-IEMA. All IEMA functionalized oligomers provided a degree of end group functionalization above 95% (investigated by NMR spectroscopy) and in this way were qualified for the hydrogel synthesis. Furthermore, the oligomers had a $M_n$ of $4000 \pm 400$ g mol$^{-1}$ for OTHF-IEMA, $2300 \pm 200$ g mol$^{-1}$ for OCL-IEMA, and $2800 \pm 300$ g mol$^{-1}$ for OPDL-IEMA which were determined by GPC and showed a melting temperature ($T_m$) of $23 \pm 2$ °C, $48 \pm 2$ °C, and $88 \pm 1$ °C. As the detected melting transitions exhibited a difference of at least $20^\circ C$, the semi-crystalline oligomers might be suitable for the generation of distinct separated $T_m$s in hydrogels.

Quadruple-shape hydrogels were synthesized by radical *in situ* copolymerization of OTHF-IEMA, OCL-IEMA, and OPDL-IEMA as switching segments (integrated as side chains), NVP as backbone forming swelling segment, and OEGDMA as crosslinker (0.5 mol% relative to OTHF, OCL, OPDL, and NVP). After swelling the obtained polymer networks with water to equilibrium, hydrogels with oligomeric side chains could be obtained. A series of hydrogels denominated as $T(a)C(b)P(c)$ was designed, in which $a$ indicates the wt% of OTHF-IEMA (T), $b$ the wt% of OCL-IEMA (C), and $c$ the wt% of OPDL-IEMA (P). The remaining fraction of the sample-ID to reach 100 wt% determined the weight fraction of NVP as swelling segment. According to the described dependencies of the ratio between switching segments in hydrogels and the swelling capacity (decreases with increasing content of hydrophobic switching segments) [16], a low content of the switching segments was required, which should nevertheless be sufficient to enable a high fixation capability of deformed shapes. As OPDL presents the switching segment providing the strongest hydrophobic character, a content of 10 wt% for OPDL was used for hydrogel synthesis. OCL as second switching segment, which exhibits a lower hydrophobic character in comparison to OPDL, was incorporated in the hydrogel matrix with 20 wt%. The third possible switching segment OTHF exhibits a more pronounced hydrophilic character compared to OCL and OPDL. For this reason different mass fractions of OTHF (20 wt%--50 wt%) were incorporated in the hydrogel matrix as the minimum content to enable the generation of an adequate number of crystalline domains in an aqueous environment was difficult to predict. Accordingly, the optimum OTHF wt% with regard to shape-memory performance and swelling capacity could be identified.

The designed hydrogels exhibited a homogeneous appearance, which was investigated by means of light microscopy measurements in the bright-field mode (figure 1 left) and using polarized light (figure 1 right). In the bright-field mode, regions of a more transparent (associated to swelling areas) and regions with a darker appearance (related to areas with a lower swelling capacity) were distributed uniformly within the polymeric network. When the measurements were performed with polarized light, crystalline domains as birefringent objects can be visualized with a
bright appearance as demonstrated in figure 1 right. Here it was detected that the hydrogels included areas with crystalline fractions, which exhibited sizes in the range from 5 μm up to 50 μm and which were distributed through the whole hydrogel matrix.

Furthermore, a high yield for the thermally-induced crosslinking reaction was obtained for the whole series of polymer networks as reflected by the high gel content ($G_c \geq 92\%$) as presented in table 1. The volumetric degree of swelling in water $Q$ of the hydrophilic polymer networks was determined at 5 °C (all switching segments are in the semi-crystalline state) and at 90 °C (amorphous state of switching segments). As the detected $Q$ was almost higher than 300 vol%, all polymeric systems could be considered as hydrogels according to the definition [20]. The state of the switching segments (semi-crystalline or amorphous) exhibited no influence on the swelling capacity in the equilibrium state and in this way, an influence of swelling effects on macroscopic movements of the SMHs could be excluded. Hence, phase separated hydrophobic domains were realized in the hydrogel matrix, when the oligomeric precursors were integrated as side chains. These hydrophobic domains generated physical crosslinks by crystallization and enabled the suppression of an additional water uptake even in the amorphous state by providing a similar behavior like oil in water droplets after rearrangement of the polymer chains induced by shape transformation. In addition, amorphous oligomeric side chains could be able to generate entanglements, which would also limit an increasing swelling behavior. The wt% of the hydrophobic side chains influenced $Q$ significantly. Here, $Q$ decreased as function of the OTHF content from 450 vol% for T(20)C(20)P(10) to 320 vol% for T(50)C(20)P(10) at 5 °C. This decrease was related to the increasing hydrophilic character when the OTHF amount was increased, which would reduce the hydrophilic character of the whole polymeric network.

### 3.2. Thermal and thermomechanical characteristics of hydrogels

The presence of different melting transitions generated by the three integrated switching segments OTHF, OCL, and OPDL in SMHs was explored by DSC of samples swollen until equilibrium in water. The thermal analysis of swollen networks exhibited three melting events with $T_m$ between 24 °C–26 °C, 48–50 °C, and between 85 °C–87 °C, which were attributed to the different melting domains of OTHF, OCL, and OPDL (figure 2). Glass transitions ($T_g$) within the hydrogel caused by the oligomeric side chains were not detected, because the applied heating and cooling range was limited by water as swelling medium (temperature range 0 °C–100 °C). The obtained distinct separated melting transitions indicated the absence of co-crystallization and the formation of segregated domains as the oligomeric precursors OTHF-IEMA, OCL-IEMA, and OPDL-IEMA (utilized for hydrogel synthesis) provided melting transitions about 25 ± 1 °C, 50 ± 1 °C, and 88 ± 1 °C respectively. The thermal properties of the hydrogels were furthermore almost constant as function of the OTHF wt%. In case of T(20)C(20)P(10), the transition from a semi-crystalline to an amorphous phase could not be detected for OTHF segments. This result was attributed to the distribution of side chains in the random polymeric network, whereby probably not enough OTHF chains can interact with each other when the OTHF content is low and in this way could form no or only a marginal number of crystalline OTHF domains. In addition, OTHF has a higher hydrophilic character in comparison to OCL and OTHF. For this reason, the crystallization capacity is lower and a higher content is needed to create semi-crystalline areas. Nonetheless, all other SMHs presented the three required melting transitions, which could enable the fixation of three temporary shapes utilizing crystalline domains as temporary crosslinks with 5 °C, 30 °C, 60 °C, and 90 °C as possible temperatures required for the programming and recovery process.

As the state of crystallizable side chains (semi-crystalline or amorphous) can influence the mechanical properties of the hydrogels, shear oscillation measurements were performed on the series of hydrogels. In figure 3, the measured shear modulus G in a temperature interval between 15 °C and 95 °C is presented for the hydrogels. Here, the SMHs exhibited three different transitions as illustrated by the first derivative for the example of T(50)C(20)P(10): (1) the transition from the semi-crystalline to the amorphous state of OTHF segments, (2) the melting transition of OCL as second side chain, and (3) the transition to a complete amorphous state of the hydrogel when also OPDL was molten. Here, the temperatures of the three transitions strongly correlated to the determined $T_{ms}$ in the designed hydrogels.

At 15 °C, SMHs presented shear moduli ranging from 170 to 550 kPa, whereby an increase of the OTHF wt% raised G as a result of the higher content of crystalline fractions (equitable with an increasing number of temporary crosslinks) and a reduced swelling capacity. When the temperature was increased to 30 °C, crystalline fractions generated by OTHF were attributed to the different melting domains of OTHF, OCL, and OPDL (figure 2). Glass transitions ($T_g$) within the hydrogel caused by the oligomeric side chains were not detected, because the applied heating and cooling range was limited by water as swelling medium (temperature range 0 °C–100 °C). The obtained distinct separated melting transitions indicated the absence of co-crystallization and the formation of segregated domains as the oligomeric precursors OTHF-IEMA, OCL-IEMA, and OPDL-IEMA (utilized for hydrogel synthesis) provided melting transitions about 25 ± 1 °C, 50 ± 1 °C, and 88 ± 1 °C respectively. The thermal properties of the hydrogels were furthermore almost constant as function of the OTHF wt%. In case of T(20)C(20)P(10), the transition from a semi-crystalline to an amorphous phase could not be detected for OTHF segments. This result was attributed to the distribution of side chains in the random polymeric network, whereby probably not enough OTHF chains can interact with each other when the OTHF content is low and in this way could form no or only a marginal number of crystalline OTHF domains. In addition, OTHF has a higher hydrophilic character in comparison to OCL and OTHF. For this reason, the crystallization capacity is lower and a higher content is needed to create semi-crystalline areas. Nonetheless, all other SMHs presented the three required melting transitions, which could enable the fixation of three temporary shapes utilizing crystalline domains as temporary crosslinks with 5 °C, 30 °C, 60 °C, and 90 °C as possible temperatures required for the programming and recovery process.

### Table 1. Gel content ($G_c$) and volumetric degree of swelling $Q$ of the series of hydrogels.

| Sample-ID* | $G_c$ [%] | $Q$ [vol%] at 5 °C | $Q$ [vol%] at 90 °C |
|------------|-----------|--------------------|--------------------|
| T(20)C(20)P(10) | 93 ± 2 | 450 ± 40 | 430 ± 70 |
| T(30)C(20)P(10) | 94 ± 4 | 430 ± 50 | 410 ± 60 |
| T(40)C(20)P(10) | 92 ± 4 | 390 ± 60 | 370 ± 60 |
| T(50)C(20)P(10) | 96 ± 1 | 320 ± 30 | 350 ± 50 |

*Sample ID T(a)C(b)P(c): $a$ indicates the wt% of OTHF-IEMA (T), $b$ the wt% of OCL-IEMA (C), and $c$ the wt% of OPDL-IEMA (P).
disappeared resulting in a reduction of $G$ with moduli between 150 and 340 kPa. A continuing decrease in stiffness was also detected when the temperature was increased to $60\, ^\circ C$ ($G$ between 20 and 100 kPa) and $90\, ^\circ C$ ($G$ between 7 and 18 kPa) indicating the dissolution first of crystalline structures provided by OCL and subsequently by OPDL as side chains.

3.3. Quadruple-shape effect in hydrogels

In order to investigate the shape-memory performance of SMHs including three different switching segments, the elasticity of the hydrogels required for the programming procedure of three different shapes was investigated by tensile tests. Here, a maximum elongation at break ($\varepsilon_b$) of 230% was obtained at $90\, ^\circ C$ and $\varepsilon_b$ decreased to 100% when the temperature of experiment was decreased to $30\, ^\circ C$. For this reason hydrogels were programmed to an elongation of 50% at $90\, ^\circ C$, 75% at $60\, ^\circ C$, and 100% at $30\, ^\circ C$. The quadruple-shape capability of the hydrogels was investigated by cyclic thermomechanical experiments utilizing a tensile tester, whereby the shape fixity ratios ($R_f$) from the permanent shape A to the first temporary shape B ($R_f(A\rightarrow B)$) at $60\, ^\circ C$, the second temporary shape C ($R_f(B\rightarrow C)$) at $30\, ^\circ C$, and the third temporary shape D ($R_f(C\rightarrow D)$) at $5\, ^\circ C$ were determined. Therefore, the SMHs were heated to $90\, ^\circ C$ (amorphous state of the hydrogels) and were deformed to $\varepsilon_2^{\text{load}} = 50\%$. Subsequently, when the temperature was reduced to $60\, ^\circ C$, the crystallization of OPDL side chains was enabled. This created temporary crosslinks stabilized the applied deformation and when the external stress was released, the temporary shape B was obtained. The $R_f(A\rightarrow B)$ was obtained between 84% and 91% and an influence of the OTHF wt% was not detected (figure 4). The second temporary shape was achieved when the hydrogels were deformed to $\varepsilon_3^{\text{load}} = 75\%$ at $60\, ^\circ C$ and cooled to $30\, ^\circ C$ to realize the generation of temporary crosslinks by means of OCL crystallization. The release of the external stress resulted in the formation of shape C. Here, $R_f(B\rightarrow C)$ ranging from 78% to 89% independent on the OTHF content were obtained. Finally, at $30\, ^\circ C$ the hydrogels were elongated to $\varepsilon_4^{\text{load}} = 100\%$, cooled to $5\, ^\circ C$, and after release of the external stress the third temporary shape D was achieved.
Figure 4. Shape fixity ratios ($R_f$) and shape recovery ratios ($R_r$) of quadruple-shape hydrogels. Left: Fixation of three different temporary shapes as function of the OTHF wt% with $R_f$($A$–$B$) ($\bullet$) at 60 °C, $R_f$($B$–$C$) ($\circ$) at 30 °C, and $R_f$($C$–$D$) ($\star$) at 5 °C. Right: Recovery of the temporary shapes and the permanent shape with $R_r$($D$–$C$) ($\bullet$) at 30 °C, $R_r$($C$–$B$) ($\circ$) at 60 °C, and $R_r$($B$–$A$) ($\star$) at 90 °C.

The different temporary shapes C and B, and the permanent shape A could be recovered by increasing the temperature from 5 °C to 90 °C. The recovery of the temporary shape C was observed at 30 °C as result of the release of crystalline OTHF domains with $R_r$($D$–$C$) between 16% and 89%. Here, the formation of oil in water droplets based on OTHF (amorphous state) and the ability of oligomeric chains to form entanglements could counteract a complete shape recovery as the driving force of the shape transformation needs to overcome these physical netpoints. Furthermore, the phenomenon of an incomplete recovery might also be attributed to the ratio between physical crosslinks generated by the three different switching segments and a potential molecular rearrangement of crystalline OCL and OTHF domains at 5 °C. Here, the contribution of OTHF crystallization in the hydrogel T(20)C(20)P(10) for the fixation of the temporary shape D might be lower in comparison to the contribution of a cold drawing induced fixation by means of crystalline fractions of OCL and OPDL. As result, the cold drawing of semi-crystalline domains, which is known to contribute to the fixation of a temporary shape, would counteract to the entropy elastic recovery of shape C at a temperature below the melting transition of OCL and OPDL. When the content of OTHF was increased to 50 wt%, the contribution of cold drawn domains in comparison to physical OTHF crosslinks was reduced, whereby $R_r$($D$–$C$) was mainly driven by the release of crystalline fraction of OTHF. At a temperature of 60 °C, the temporary shape B was obtained with $R_r$($C$–$B$) in the range from 58 to 74%. Here, an influence of the OTHF content could be excluded. As also for the fixation of the temporary shape B temporary crosslinks as result of OPDL crystallization could be drawn at 60 °C, a complete recovery was not obtained. The geometry change to the permanent shape of the designed hydrogels was obtained when the temperature was increased to 90 °C. At this temperature all physical crosslinks were dissolved and only permanent crosslinks as result of the radical polymerization prevented the complete dissolution of the SMHs. Relatively constant values for $R_r$($B$–$A$) between 90% and 96% could be realized.

The quadruple-shape effect in hydrogels is demonstrated with the example of T(40)C(20)P(10) in figure 5. Here, the permanent shape, a geometric constructed pyramid (shape A) was obtained by synthesis in the presence of a 3D printed template (figure 6) based on water-soluble polymers, which were removed by dissolution. The pyramid was deformed by bending two lateral areas at 90 °C. When the temperature was cooled to 60 °C, shape B was fixed by means of the formation of physical OPDL crosslinks. Subsequently, the other lateral areas of the hydrogel were deformed, whereby this deformation was stabilized when the temperature was decreased to 30 °C (shape C). At this temperature, the generation of crystalline domains from the OCL side chains enabled the fixation process. Finally, the subsequent bending of all surface areas at 30 °C, followed by a reduction of temperature to 5 °C resulted into shape D as also temporary crosslinks of OTHF could be created. The stepwise increase in temperature from 5 °C to 30 °C, 60 °C, and 90 °C induced the macroscopic movements of the hydrogel. As different geometric information was implemented in the hydrogel matrix, the hydrogel with four deformed and two deformed lateral areas as temporary shapes (shape C and shape B) and the pyramid as permanent shape (shape A) were recovered. Here, the directed movements were induced by the release of temporary crosslinks and the entropy elasticity of the polymeric network.
4. Conclusion

Temperature-sensitive hydrogels capable of a quadruple-shape effect as new record for directed movements induced by heat were designed as swellable polymer networks with side chains from OTHF, OCL, and OPDL as three different semi-crystalline switching segments. Directed movements independent of swelling effects could be implemented as the integration of switching segments as side chains enabled the formation of segregated phases serving as thermo-sensitive switches. The hydrogels provided three different thermal transitions caused by the melting of the semi-crystalline segments between 24°C–26°C for OTHF, 48°C–50°C for OCL, and between 85°C–87°C for OPDL. The hydrogels exhibited a sufficient overall elasticity for three deformations as required for the programming procedure of a quadruple-shape effect. Here, high fixation ratios can be obtained when the content of switching segments is increased, but simultaneously the swelling capacity is decreased. Accordingly, the weight fraction of switching segments with a strong hydrophobic character (e.g. OPDL and OCL) had to be high enough to enable the fixation of a temporary shape and simultaneously should not dominate the properties of the polymeric material in order to enable a sufficient swelling behavior. The temporary shapes C, B, and the permanent shape A could be obtained when the corresponding temporary crosslinks were released. As the programming process included stepwise deformations at different temperatures, cold drawn domains of already existing semi-crystalline fractions were created. This phenomenon was reflected by the obtained incomplete recovery of temporary shape C when a low content of OTHF was used. Hence, thermo-mechanical treatment led to an interference of temporary crosslinks, which increases with increasing number of different switching segments, whereby the performance is reduced. However, directed movements in hydrogels based on semi-crystalline switching segments are not limited to the reported triple-shape effect, in this work a new record, the design of quadruple-shape hydrogels, was realized when heat as easy stimulus was applied. Therefore, fascinating candidate materials with multiple-shape shifts as recommended for tightening materials for pipelines, which induce a required fastening when the...
temperature is increased, sieves enabling purification of desalination plants or selective dumps for a temperature controlled dosing of detergents could be realized.

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