Anisotropy Effects in the Shape-Memory Performance of Polymer Foams

Tilman Sauter, Karl Kratz, Samy Madbouly, Frank Klein, Matthias Heuchel, and Andreas Lendlein*

Isotropic and anisotropic shape-memory polymer foams are prepared by supercritical carbon dioxide foaming from a multiblock copolymer (PDLC) consisting of poly(ε-pentadecalactone) and poly(ε-caprolactone) segments. Analysis by micro-computed tomography reveals for the anisotropic PDLC foam cells a high shape anisotropy ratio of $R = 1.72 \pm 0.62$ with a corresponding Young’s compression moduli ratio between longitudinal and transversal direction of 4.3. The experimental compression data in the linear elastic range can be well described by the anisotropic open foam model of Gibson and Ashby. A micro-morphological analysis for single pores using scanning electron microscopy images permits the correlation between the macroscopic stress-compression behavior and microscale structural changes.

1. Introduction

Compact elastomeric shape-memory polymers (SMPs) as stimuli-responsive materials[1–3] allow in simple words the fixation and recovery of extended ($L + \Delta L$) shapes of a sample with original length $L$. The elastic compression ($L - \Delta L$) of a sample with original length $L$ can better be realized in foam shape. Generally, foams have a higher compressibility, even if mechanical properties (stiffness and strength) are generally reduced. Combined with low density and sufficient restoring force, SMP foams have a great potential in applications from the biomedical field to aerospace.[6–8] Polymer foams are used as shock or noise absorbing, light weight, and insulating materials.[9,10] Currently, SMP foams are tested in aerospace for the design of small-size actuators for self-deployable structures under microgravity.[8] In the biomedical field, SMP foams were proposed for treatment of intracranial aneurysm, where the foams may better fill the entire aneurysm cavity, and they are discussed for drug delivery, as biosensors. Very recently, biodegradable SMP foams with clinically applicable thermal properties and the ability to quickly initiate blood clotting are discussed as an effective hemostatic device.[11] Concerning the actual foaming process, in polyurethane-based SMP foams water is applied as blowing agent.[12,13] Another foaming technology uses supercritical carbon dioxide (scCO2).[14] scCO2 can serve as plasticizer, which allows the processing of polymers, for example, in an extruder, which would otherwise be too fragile to withstand the mechanical stresses and the operating temperatures of a standard extrusion process. In addition, CO2 can easily be removed and is advantageous in terms of medical applications compared to other methods that involve the use and removal of toxic organic solvents.

Polymeric foams can be tailored in their properties by their foam density,[15] pore size,[16] the pore size distribution,[17] as well as open[15–26] and closed pore structures.[21,22] The influence of the foam microstructure on its mechanical or shape-memory properties is related to the same architectural principles that apply on the macroscale (elastostatic, e.g. triangular load bearing structures in cranes). In this respect, it is hypothesized that the pore geometry can influence the microscopic deformation behavior of the foam and in this way determining its macroscopic mechanical and shape-memory properties. Specifically, an anisotropic pore geometry, which comprises at least different extensions in two of the three possible $x$, $y$, and $z$ directions ($l_x \neq l_y \neq l_z$), should result in a different structural performance when tested in transverse ($x$–$y$) and axial or longitudinal ($z$–$x$) foam direction. Microstructural design approaches in SMPs may specifically allow to influence the shape-memory effect for programmed expansion. The proposed strategy comprises i) the choice of a suitable microstructural parameter to

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influence shape-memory properties, ii) the creation of a fabrication scheme that permits variation of one geometry parameter while keeping other geometrical features constant. iii) Thirdly, the SMP foam is evaluated macroscopically with respect to the macroscopic functions. Finally, iv) the microscopic in situ evaluation should unravel the microstructural contribution toward the observed macroscopic effects.

In this study these four steps of a knowledge-based SMP foam design shall be performed on the illustrative example of the pore anisotropy. As suitable design parameter i) the pore geometry may be altered toward a higher pore aspect or anisotropy ratio $R = \frac{l_y}{l_x}$, which should result in an increased energy uptake during compression along $l_x$ as compared to $l_y$ or $l_z$. This assumption is based on considering the pore as a simple spring, where its compression along a longer path causes a higher spring energy. This, in turn, might permit specific tuning of the shape-recovery (expansion) stress $\sigma_{\text{max}}$ as well as the shape-recovery ratio $R_{\text{shr}}$.

2. Results and Discussion

2.1. Anisotropic and Isotropic PDLCL Foams

scCO$_2$ was chosen as sustainable foaming technique$^{[21-25]}$ to prepare SMP foams with tailored morphologies from the biodegradable multiblock copolymer PDLCL with reported excellent dual-shape and temperature-memory properties.$^{[26-28]}$ PDLCL is composed of crystallizable poly(α-pentadecalactone) (PPDL) hard and poly(ε-caprolactone) (PCL) switching segments. It exhibits two distinct well separated melting transitions associated with PDLCL-AN and PCL, respectively.$^{[29]}$ Crystallites were strongly aligned along the $z$-direction in PDLCL-AN ($-70^\circ < \chi < -90^\circ$) according to results of wide-angle X-ray scattering (WAXS), while in the transversal direction (TD) the scattering remained isotropic indicating that there is no preferred orientation of the PPDL and PCL crystallites in the $x$-$y$ plane (Figure S1, Supporting Information).

PDLCL-IS exhibited isotropic WAXS profiles in both longitudinal and TDs. Compression tests at ambient temperature revealed an initial strong elastic stress increase in the longitudinal direction (LD) of PDLCL-AN with a Young’s modulus of $E_L = 1.3 \pm 0.2$ MPa, which was followed by a high stress plateau until 50% compressive strain, whereas the cell walls collapsed and densification occurred. By contrast, compression of PDLCL-AN along the TD led to a reduced and rather linear stress increase up to 50% compressive strain ($E_T = 0.3 \pm 0.1$ MPa), where subsequently densification caused a strong increase in stress (Figure 1-I, VII). At a compressive strain of $\varepsilon = 50\%$ the uptaken energy is threefold higher along the longitudinal as compared to the TD. By contrast, compression of the isotropic foam (PDLCL-IS) resulted in an almost identical stress-strain behavior in the transversal and LD with $E_T = E_L = 0.6$ MPa.

The linear elastic properties of both foams should correspond to their experimentally derived morphological properties. The relation can be constructed via the foam model for anisotropic porous structures (Figure 2) derived by Gibson and Ashby,$^{[23]}$ which was experimentally verified.$^{[30]}$

For an anisotropic open pore foam, with struts of thickness $t$, and lengths $h$ and $l$ in the LD and transverse directions (TD), respectively, they calculated the respective modulus values. For the moduli in LD and TD the following equations were derived for the linear stress $\sigma$ versus strain $\varepsilon$ range:

$$E_{\text{LD}} = \frac{\sigma_{\text{LD}}}{\varepsilon_{\text{LD}}} = C \cdot \frac{E_s}{2} \left(\frac{t}{l}\right)^3 \frac{h}{l}$$  \hspace{1cm} (1)

$$E_{\text{TD}} = \frac{\sigma_{\text{TD}}}{\varepsilon_{\text{TD}}} = C \cdot \frac{E_s}{2} \left(\frac{t}{l}\right)^3 \frac{h}{l} \left[1 + \left(\frac{t}{h}\right)^3\right]$$  \hspace{1cm} (2)

where $E_s$ is the modulus of the solid, $I$ is the second moment of area of the cell edge, and where $C$ is a constant. The ratio between longitudinal and transverse modulus Equations (1) and (2) can be related to the degree of anisotropy $R = h/l$.

$$\frac{E_{\text{LD}}}{E_{\text{TD}}} = \frac{2R^3}{1 + \left(1/R^3\right)}$$  \hspace{1cm} (3)

The experimentally determined $(E_{\text{LD}}/E_{\text{TD}})_{\text{exp}}$ ratio was $\approx 4.3$, which results from Young’s moduli of PDLCL-AN of $E_L = 1.3 \pm 0.2$ MPa and $E_T = 0.3 \pm 0.1$ MPa. This would correspond via Equation (3) to an experimental degree of anisotropy of $R_{\text{exp}} = 1.63$. This value agrees very well with the µCT-determined shape anisotropy for this foam of $R = 1.72 \pm 0.62$. For the isotropic

All foams showed a high degree of porosity of $89 \pm 4\%$, whereby $50-60\%$ of the pores were accessible by nitrogen as determined by pycnometry measurements. An average wall thickness of $6-7 \mu$m was observed for all foams (Figure 1-III, VI). Crystallites were strongly aligned along the $z$-direction in PDLCL-AN ($-70^\circ < \chi < -90^\circ$) according to results of wide-angle X-ray scattering (WAXS), while in the transversal direction (TD) the scattering remained isotropic indicating that there is no preferred orientation of the PPDL and PCL crystallites in the $x$-$y$ plane (Figure S1, Supporting Information).

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$$E_{\text{TD}} = \frac{\sigma_{\text{TD}}}{\varepsilon_{\text{TD}}} = C \cdot \frac{E_s}{2} \left(\frac{t}{l}\right)^3 \frac{h}{l} \left[1 + \left(\frac{t}{h}\right)^3\right]$$  \hspace{1cm} (2)

where $E_s$ is the modulus of the solid, $I$ is the second moment of area of the cell edge, and where $C$ is a constant. The ratio between longitudinal and transverse modulus Equations (1) and (2) can be related to the degree of anisotropy $R = h/l$.

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foam sample PDLCL-IS, the experimental \((E_{LD}/E_{TD})_{exp}\) ratio was 1.0, in agreement with the structural value of \(R = 1.03 \pm 0.23\). Based on the anisotropic open foam model, the experimental compression data in the linear elastic range can be well described, as shown in Figure 3.

The model description is based on Equations (1) and (2). For the structural input parameters of the asymmetric open foam model [strut thickness \(t = 6.5\) µm, and lengths \(h\) (LD) and \(l\) (TD)] the open mentioned mean values from the µCT analysis were used (Table S2, Supporting Information). For the Young’s modulus of the solid PDLCL the experimental value \(E_s = 55\) MPa was taken. The proportionality constant \(C\) was estimated with isotropic foam data to a value of \(1.7 \times 10^5\), and used for the calculation for the anisotropic PDLCL foam. The good description of the experimental data shows that a modeling of the linear elastic mechanical properties of both foams was possibly based on size parameters, which were determined from µCT.

Anisotropic mechanical properties induced by structural anisotropy were similarly observed by Mathieu et al., who found a significant higher stiffness along the CO2 expansion direction as compared to the perpendicular direction. The influence of microstructural anisotropy on the macroscopic mechanical properties could also be confirmed theoretically by Silva et al.,

Figure 1. Overview of scCO2 foaming strategy, the resulting pore morphologies, and the results of the compression test for two PDLCL foams. Upper part A) Axial gas release (I) resulted in an anisotropic foam PDLCL-AN with elongated cells along the axial foaming direction (\(z-x\): (II) and SEM image (III)) compared to the transverse foaming direction (\(x-y\): (V) and SEM image (VI)). Mechanical compression experiments at ambient temperature are shown for both directions in (IV) and enlarged for the linear elastic compression range up to \(\varepsilon = 6\%\) in (VII). The lower part B) shows the corresponding data for the isotropic foam PDLCL-IS prepared with homogeneous gas flow in all directions.
who found an increase in relative modulus by increase in microstructural anisotropy.[32] Anisotropy effects on stiffness and strength for low density polymer foams could be modeled with the rectangular unit cell model used by us, as well as with a more advanced tetradecahedron (Kelvin) cell model.[33] A simulation of stress-strain data at higher compressive strains for anisotropic polymeric foams was based on orientation distribution of foam struts.[34] The model considers that with increasing strain, a high number of individual struts, which tend to align parallelly to the loading axis, become unstable and buckle elastically or plasticly, exhibiting the plateau region. A deeper understanding of structural anisotropy on the mechanical behavior was tried by combination of a µCT characterization of foams to build a 3D representative volume element (RVE) and calculation of the mechanical response with finite element analysis (FEA) of the RVE in perpendicular directions.[35] FEA was also used in an anisotropic elastic damage constitutive model.[36] But still the accurate description of the plateau regime is a challenge.[37] The anisotropic elastoplastic deformation behavior of polymeric foams in compression was recently quite successful simulated with FEA, based on observed µCT images, which were used to fit an elongated rhombic dodecahedron as model to mimic the 3D structure of the anisotropic foams.[38]

2.2. Macroscopic View on Shape-Memory Properties of PDLCL Foams

The influence of the pore geometry on the macroscopic shape-memory properties of the foam was evaluated by cyclic thermomechanical compression tests in the PDLCL-AN foam. Here stress, strain, and temperature were measured continuously over time. Figure 4 shows the temperature dependence of the relative foam size \((1 - \varepsilon)\) [%] for PDLCL-AN, compressed along the longitudinal and transversal foaming directions. The sample was heated up to \(T_{\text{deform}} = 60^\circ\text{C}\) and compressed to \(\varepsilon_m = 50\%\) and then cooled down quickly to \(T_{\text{low}} = 0\,^\circ\text{C}\) and afterward heated under stress-free conditions to \(T_{\text{high}} = 75\,^\circ\text{C}\).

Although the applied compression \(\varepsilon_m\) was 50% for each measurement, a considerable increase in the value of the

Figure 2. Model of an axisymmetric unit cell of a 3D-foam with a shape anisotropy ratio, \(R = h/l\) of 1.5. Reproduced with permission.\(^{[25]}\) Copyright 1988, Chapman and Hall Ltd.

Figure 3. Model description of experimental stress versus compression strain data (open symbols) in the linear elastic range for PDLCL-AN and PDLCL-IS in longitudinal (LD) and TD. The structural parameters for the asymmetric open foam model for strut thickness \(t\), and lengths \(h\) (LD) and \(l\) (TD) were obtained from µCT analysis. Calculation (lines with points) are based on Equations (1) and (2).

Figure 4. Cyclic thermomechanical shape-memory experiments of the anisotropic foam PDLCL-AN by compression to \(\varepsilon_m = 50\%\) at \(T_{\text{deform}} = 60\,^\circ\text{C}\), cooling to \(T_{\text{low}} = 0\,^\circ\text{C}\), and recovery under stress-free conditions to \(T_{\text{high}} = 75\,^\circ\text{C}\). A) in LD; B) in TD.
resultant compression after cooling the sample to 0 °C was clearly observed. This additional increase in the compression is attributed to the very fast crystallization process of PCL, which leads to a highly ordered and compact structure and consequently induces an additional compression to the initial value. It is also noteworthy that the foam measured in TD has an additional compression value of about 10%, which is more than twice the value that was detected for LD (4%). This is most likely due to the collapses of the pores that can generate more compact structures when the sample is compressed in the TD compared to the longitudinal one. The compressed foam starts to recover by releasing the applied external compression and heating up to $T_{\text{high}} = 75$ °C. The recovery of the original shape is attributed to the fact that with increasing temperature the foam can regain the entropy that was lost during the compression step. For compression in TD, this recovery is lower compared to LD.

To investigate the shape-memory properties of the PDLCL-AN foam quantitatively, the shape-fixity ratio $R_f$ as well as the absolute shape-recovery ratio $R_{\text{abs}}$ were calculated according to Equations (4) and (5) (Experimental Section). In the shape-memory creation procedure (SMCP) along the longitudinal and TD, the foam was heated to $T_{\text{high}} = 75$ °C, then uniaxially compressed and subsequently cooled to $T_{\text{flow}} = 0$ °C fixing the temporary shape. $R_f$ could be obtained after unloading, which was $R_f > 100\%$ due to the mentioned crystallization of the PCL segments during cooling causing a further contraction of the foam. The main focus in this study, however, was placed on the recovery of the PDLCL-AN foam under stress-free conditions to quantify the shape-recovery ratio $R_{\text{abs}}$ and under constant strain conditions to assess the maximum recovery stress $\sigma_{\text{max}}$. The comparative results for the shape-memory properties depending on the pore geometry are displayed in a demonstration experiment in Figure 5.

The original shape of PDLCL-AN was almost fully recovered for the foam programmed in the LD with an absolute shape recovery $R_{\text{abs}} = 89 \pm 1\%$, while recovery in TD resulted in a significantly lower $R_{\text{abs}} = 40\%$ as displayed in Figure 5A as well as Table S3, Supporting Information. Independent from the programming direction, similar characteristic switching temperatures ($T_{\text{sw}}$) were obtained with $T_{\text{sw,LD}} = 73 \pm 1$ °C and $T_{\text{sw,TD}} = 70 \pm 3$ °C. Under constant strain recovery conditions, a maximum recovery stress ($\sigma_{\text{max}}$) of 63 kPa could be generated for PDLCL-AN along the LD, whereas $\sigma_{\text{max}}$ remained at 41 kPa for the TD (Figure 5B). The characteristic temperature ($T_{\sigma_{\text{max}}}$), at which $\sigma_{\text{max}}$ is observed, was $42$ °C for both programming directions. A bell-shaped curve was obtained corresponding to an increase in stress until $\sigma_{\text{max}}$ is reached, which represents an equilibrium state where entropy elasticity driven retracting forces are overcome by softening of the polymer. In Figure 5C,D as well as in Movie S1, Supporting Information a weight lifting experiment is shown. During heating a 200 g weight was lifted higher along the longitudinal foaming direction releasing roughly double as much energy (12 mJ) with respect to the transversal (6 mJ) direction. The isotropic PDLCL-IS foam exhibited almost identical shape-memory properties depending on the loading direction (Figure S3, Supporting Information).

2.3. Microscopic View on Shape-Memory Properties of PDLCL Foams

Significant differences in the macroscopic properties ($R_{\text{abs}}$ and $\sigma_{\text{max}}$) prompted therefore a microscopic evaluation of the PDLCL-AN foam. As characterization method for assessing shape-memory properties, an in situ morphological analysis of the foam cross-section based on scanning electron microscopy (SEM) images has been developed. A temperature-controlled micro-bench vise as shown in Figure S4, Supporting Information was applied to program PDLCL foam samples in the temporary shape and to observe its stress-free recovery. SEM pictures were obtained from the original, temporary, as well as the recovered foam cross-section (Figure 6).

The single images demonstrate the morphology of isotropic and anisotropic (compression along the longitudinal foaming direction) for uncompressed, compressed, and completely recovered foams. A significant deformation of the pores along the compression direction can be identified particularly in the area, where the compression is applied. In case most porosity was squeezed out and a highly compact structure was obtained. No significant changes in the pores near the medial of the foam could be determined. Although the compression produces compact or almost solid-like structure (in the area of the applied compression), most of these pores recover to their original shapes with a considerable reduction in the pore size. This experimental fact is an evidence for the recovery of the foam structure and its anisotropic morphology and mechanical properties during the thermally induced shape recovery process. It is also noteworthy that the recovery in each case reaches $=80\%$ and the average pore size reduces by $20\%$ in this experiment.

The SEM images allow also an observation of individual cells and therefore the analysis of the foam height (macro: ma) as well as the (single) pore height (micro: mi), area and an estimate of the 2D perimeter (see Figure 7).

For PDLCL-AN, the pore height change was determined in relation to an almost constant perimeter throughout the different SMCP states (longitudinal: 76 ± 15%; transversal: 82 ± 5%). Compression strain of the foam to $\varepsilon = 50\%$ led to a comparable compression of the pores in the LD, while only a reduced compression of the pores ($\approx30\%$) occurred if tested along the TD. Furthermore, high shape-fixity ratios $R_{\text{f,ma}}$ and $R_{\text{f,mi}}$ for the macro- and microscale of almost 100% could be obtained in both testing directions, which is in excellent agreement with the results from the cyclic thermo-mechanical experiments. An almost complete shape recovery was achieved for PDLCL-AN longitudinally ($R_{\text{abs,ma}} = 91 \pm 3\%$) exhibiting also a high single pore recovery ($R_{\text{abs,mi}} = 88 \pm 6\%$). In contrast, the recovery of transversally programmed foam was found to be significantly lower on both levels ($R_{\text{abs,ma}} = 22 \pm 5\%$; $R_{\text{abs,mi}} = 18 \pm 7\%$), which was in accordance with the tendency observed in the cyclic thermo-mechanical experiments. These results suggest that the pore recovery is predominating driving the recovery of the foam, while only a minor contribution of about 3% of the shape change takes place in the bulk. The results for the microscopic analysis are depicted in Figure 7 and Table S4, Supporting Information.
Figure 5. Demonstration of macroscopic cyclic thermomechanical examination of the PDLCL-AN in transversal (left) and LD (right). A) Stress-free recovery; B) constant strain recovery; C,D) shape recovery of PDLCL-AN TD (left-A) and in LD (right-B) with 200 g load is shown from 30 °C (C) to 70 °C (D). All samples were programmed by the same SMCP: $T_{\text{deform}} = 60 ^\circ \text{C}$, $\varepsilon_m = 50\%$, $T_{\text{low}} = 0 ^\circ \text{C}$. 
Figure 6. Microscopic evaluation of the PDLCL foams during a shape memory test using SEM images for the evaluation (from top to bottom) of the initial, temporary (compressed), and recovered foam. Images are shown for PDLCL-AN along the LD, TD, and for the isotropic PDLCL-IS foam.

Figure 7. Comparison of macroscopic shape recovery values of the PDLCL-AN foam with data obtained from SEM images for single cells of the foam in TD (left) and LD (right). A) SEM evaluation of the i) original, ii) temporary, and iii) recovered foam. The arrows highlight the pore height change depending on the SMCP and stress-free recovery. B) Analysis of the respective foam height as well as of the pore height for compression strains (macroscopic: ma, dashed line) as well as of the pore height (microscopic: mi, full line) for compression, $R_f$ and $R_{abs}$. 
3. Conclusion

SMP foams composed isotropic pores with identical lengths in all three spatial directions as well as strongly anisotropic pores with a high shape-anisotropy ratio of 1.7 were achieved by using the scCO₂ foaming method. SMP foams composed of anisotropic pores exhibited direction dependent Young's moduli (Young’s modulus ratio of 4.3 between LD/TD), which was not the case for SMP foams containing isotropic pores. Depending on the foam orientation, a strong difference in the stress-free as well as constant strain recovery was observed with higher shape-recovery for the longitudinal foam direction as compared to the transversal foam direction which was confirmed by classical cyclic thermomechanical compression tests as well as by a novel microscopic in situ shape-memory experiment that allowed to investigate the foam macroscopically (foam level) and microscopically (pore level). The proposed steps in such an evaluation strategy might serve as basis guideline for in future designs of SMP foams for a broad range of potential application areas from self-expanding implants in minimally-invasive surgery to active components of the interior of space vehicles.

4. Experimental Section

**PDCL Synthesis:** PDCL was synthesized by the prepolymer method according to the procedure described in ref. [39] 600 g poly(ε-caprolactone)diol with an averaged molecular weight of \( M_n = 3000 \text{ g mol}^{-1} \) and a melting temperature of \( T_m = \text{around 58–61 °C} \) (Solvay Caprolactones, Warrington, U.K.) and 400 g poly(ε-caprolactone)diol with \( M_n = 4300 \text{ g mol}^{-1} \) and \( T_m = 98–102 \text{ °C} \) (prepared by ring-opening polymerization of \( \varepsilon \)-caprolactone with octandiol as the initiator as described in ref. [39]) were reacted with 70 g 1,6 hexamethylene diisocyanate (Fluka, Buchs, Switzerland) in 2500 mL dimethylcarbonate (Acrros Organics, Geel, Belgium) at 85 °C for 48 h. The resulting product PDCL with \( M_n = 100 \text{ 000} \text{ g mol}^{-1} \) and a polydispersity of a \( PD = 5.1 \) was obtained by precipitation in liquid \( N_2 \) and after drying in vacuum for 10 days in a yield of 99%.

**Foaming Procedure:** Prior to the foaming process, the PDCL raw material was granulated at 95 °C in a single screw extruder (Thermo Electron I/34, d = 15 mm). Details of foaming process using scCO₂ as foaming agent are described elsewhere. [40] For anisotropic foams (PDCL-AS), the PDCL granules were filled in 20 mL glass beakers (standard glass; \( \Omega: 29 \text{ mm}; \text{height: 50 mm} \) acting as foaming vessel to generate foams with aligned anisotropic pores. For the isotropic foams (PDCL-IS) a metal micro-mesh (stainless steel, 0.6 mm mesh size) was used as foaming vessel. The mesh was placed at an elevated position to allow an expansion in all three dimensions. The foaming vessel was placed in an autoclave and saturated with scCO₂ at \( T = 79 \text{ °C} \) and constant pressure (100 bar) for 30 min. [40] A depressurization rate of 25 bar s⁻¹ was applied. After saturation pressure was reached the pressure relief program was initiated and the PDCL foams were obtained.

**MicroX-Ray Computed Tomography:** The foam morphology was investigated using a µCT (CT- COMPACT, ProCon X-Ray GmbH, Garbsen, Germany). The foam was fixed on a rotary stage and scanned inside the µCT apparatus. The morphology investigation was carried out with a tungsten target and operated at a voltage of 40 kV and a current of 0.19 mA. The specimens were scanned in \( x, y, \text{and z directions} \). A CCD line array was used to detect the transmitted intensity through the sample. The X-ray beam was collimated by a slit collimator system. The distance between source and detector was fixed. The sample was rotated in 800 steps through 360° and the raw data were recorded as 3D shadow pictures. Porosity and pore geometry were quantitatively determined from the 3D µCT images. From the single pore length values \( l_1 \) in foam rise direction, and \( l_2 \) and \( l_3 \) perpendicular to this direction, first the ratios \( R_{lx} = l_1/l_2, R_{ly} = l_1/l_3, \text{and } R_{lz} = l_1/l_3 \) had been calculated, further \( R_{xy} = R_{lx}/R_{ly} \) and finally the shape-anisotropy ratio \( R = (R_{xy} + R_{ly})/2 \), where over all pores of the foam sample were averaged. For the image processing the MAVI software (Fraunhofer ITWM, Kaiserslautern, Germany) was used.

**Morphological and Mechanical Characterization:** The foam density was calculated as ratio of volume and the mass of the foam sample, while the accessible open porosity was determined by pycnometer measurements (Ultrafoam Pycnometer 1000, Quantometric Instruments, Boynton Beach, FL, USA) using nitrogen as displacement fluid. The cross-section of the foam was investigated by means of SEM (Gemini Supra 40 VP, Zeiss, Jena, Germany). The degree of crystallinity (DOC) and crystalline orientation was examined by wide WAXS experiments (D8 Discover, Bruker-AXS, Karlsruhe, Germany) at 40 kV and 40 mA (exposure time: 120 s). The detector with a distance to the sample of 150 mm was positioned at an angular position \( 2θ = 25° \) in order to cover an angular range from \( 2θ = 7.2° \text{ to } 43.5° \). The foams were cut into flat sheets (length × width × height: 1.0 × 0.5 × 0.2 mm²) with the flat side either representing the axial (along the direction of the scCO₂-flow) or transverse side (perpendicular to the direction of the scCO₂-flow) (see Figure S1, Supporting Information) and examined both equatorial as well as meridional. Integration over the whole 20-plane was performed and the peaks of the two phases (amorphous and crystalline) were fitted with Pearson VII functions. The relationship of the integrated areas determined the DOC. At an angle \( 2θ = 20.4° \) a strong crystalline peak was observed, at which integration over the angle \( \chi \) from \(-230° \text{ to } -30° \) allowed the distinction between isotropic and anisotropic crystalline orientations. The mechanical properties at ambient temperature were analysed on a standard compression tester (Instron 3345, Instron, Norwood, MA, USA). Cubic foam samples with an edge length of \( 10 \text{ mm} \) were cut and tested until failure at ambient temperature.

**Macroscopic Shape-Memory Properties:** Uniaxial cyclic thermomechanical compression experiments were applied to investigate the shape-memory properties macroscopically, where a compression tester (Z1.0, Zwick, Ulm, Germany) in combination with a thermo chamber (Eurotherm Regler, Limburg, Germany) was utilized. The foam was first heated above the melting temperature associated to PCL \( T_{m,pcl} \) to the deformation temperature \( T_{deform} = 60 \text{ °C} \), compressed to the programming compression strain \( ε = 50% \) and cooled to \( T_{raw} = 0 \text{ °C} \) while maintaining the compressive stress. After stress removal at \( T_{deform} \) the temporary fixed shape \( ε \) was obtained. Heating of the programmed samples to \( T_{rec} = 75 \text{ °C} \) was applied for recovery of the sample, whereby the change in shape up to the recovered shape \( ε \) was recorded under stress-free conditions and the evolution of the recovery stress was followed under constant compressive stress conditions, from which both the maximum recovery stress \( (σ_{max}) \) as well as the temperature at this stress value \( (T_{0,σ_{max}}) \) could be obtained. The shape-fixity ratio \( R_1 \) as well as the absolute shape-recovery ratio \( R_{abs} \) are calculated according to Equations (4) and (5):

\[
R_1 (N) = \frac{ε_p (N)}{ε_m} \times 100
\]

(4)

\[
R_{abs} (N) = \left( 1 - \frac{ε_p (N)}{ε_m} \right) \times 100
\]

(5)

**Weight Lifting Experiment:** The foam samples were programmed along axial and transverse foaming directions at \( ε = 50% \) based on the SMCP condition. A weight of 200 g was fixed on the top of each foam (own weight \( = 0.5 \text{ g} \) ) and the temperature was increased by \( 1 \text{ °C min}^{-1} \) heating rate up to \( 70 \text{ °C} \) in an electric oven. The two foams were able to lift the 200 g to different levels based on the different stress recoveries or energies that were stored in the foams during deformation.

**Microscopic In Situ Shape-Memory Experiments:** The experiments were performed with the same SMCP as for cyclic thermomechanical
experiments, while a micro-bench vise was applied to compress the sample which allowed monitoring the cross-section of the foam by SEM (Phenom G2 Pro, Phenom-World BV, Eindhoven, Netherlands) during the SMCP and the recovery under stress-free (clamps were fully opened) conditions. It was possible to observe both the change in foam height (macroscopic results) as well as the change in pore height (microscopic results) in each state, namely the original unchanged, compressed ($e_n$), temporary ($e_p$), and recovered state ($e_r$) by the image processing software ImageJ.[29]

Statistics: For the mechanical compression tests at room temperature eight foam samples were used. The uniaxial three-cycle thermomechanical compression experiments were applied to five samples. The mean pore size in different direction were obtained from 1430 pores in PDLCL-AN and 2000 objects in PDLCL-IS. In the microscopic in situ shape-memory experiments, the pore dimensions were obtained from 20 objects for every SMCP step. Error estimates for presented properties in Tables S2–S4, Supporting Information are based on these data sets.

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 the following competing financial interest(s): F.K., K.K., A.L., and S.M. are inventors of a patent related to foam molding. The authors declare the following competing financial interest(s): F.K., A.L., and S.M. are inventors of a patent related to foam molding.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
anisotropy, polymer foams, pore geometry, shape-memory polymers, structural function

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