Influence of deformation temperature on structural variation and shape-memory effect of a thermoplastic semi-crystalline multiblock copolymer

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Abstract. A multiblock copolymer termed as PCL-PIBMD, consisting of crystallizable poly(ϵ -caprolactone) (PCL) segments and crystallizable poly(3*S*-isobutyl-morpholine-2,5-dione) (PIBMD) segments, has been reported as a material showing a thermally-induced shape-memory effect. While PIBMD crystalline domains act as netpoints to determine the permanent shape, both PCL crystalline domains and PIBMD amorphous domains, which have similar transition temperatures (T_{trans}) can act as switching domains. In this work, the influence of the deformation temperature ($T_{\text{deform}} = 50$ or 20°C), which was above or below T_{trans} , on the structural changes of PCL-PIBMD during uniaxial deformation and the shape-memory properties were investigated. Furthermore, the relative contribution of crystalline PCL and PIBMD amorphous phases to the fixation of the temporary shape were distinguished by a toluene vapor treatment approach. The results indicated that at 50°C , both PCL and PIBMD amorphous phases can be orientated during deformation, resulting in thermally-induced crystals of PCL domains and joint contribution to the switching domains. In contrast at 20°C , the temporary shape was mainly fixed by PCL crystals generated via strain-induced crystallization.

Keywords: biodegradable polymers, shape-memory polymer, multiblock copolymer, polydepsipeptide

1. Introduction

Shape-memory polymers (SMPs) can be deformed from their permanent shape and temporarily fixed in a second shape. The original shape can be recovered by application of suitable external stimulus, such as e.g. heat [1–6]. Suitable molecular architectures consisting of netpoints determining the permanent shape and molecular switches fixing the temporary shape are required to enable a shape-memory effect (SME) in polymers [1–3]. Multiblock copolymers (MBCs) consisting of at least two segregated domains, thus, are considered as a versatile molecular architecture in creating SMPs [1, 2, 6–8]. Recently, a novel class of MBCs composed of crys-

tallizable poly(ϵ -caprolactone) (PCL) segments and crystallizable poly(3*S*-isobutyl-morpholin-2,5-dione) (PIBMD) segments was introduced and termed as PCL-PIBMD. It has been reported that excellent SME can be found in PCL-PIBMD with 50 wt% PIBMD segments [6–8]. In addition, while PIBMD crystals with a high melting temperature (T_{m}) of 170°C act as permanent physical netpoints, the melting temperature of PCL crystallites ($T_{\text{m,PCL}} \approx 38^\circ\text{C}$) is close to the glass transition temperature of PIBMD ($T_{\text{g,PIBMD}} \approx 42^\circ\text{C}$) domains [6–8]. Therefore, both the PCL crystalline phase and the PIBMD amorphous phase form the switching domains.

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The deformation temperature (T_{deform}) has significant effects on deformation behaviors of semi-crystalline polymers on the microscopic and macroscopic scale [9, 10], with structural variations during the deformation playing a dominant role in determining their mechanical properties [11, 12]. It also has been reported that T_{deform} can affect the SME of semi-crystalline MBCs, i.e., if the samples are deformed at a temperature lower than the thermal transition temperature (T_{trans}) of switching domains, reduction in fixity ratio (R_f) and switching temperature (T_{sw}) can be observed as well as a higher maximum stress (σ_m) is required [13–14]. Therefore, it is necessary to explore the mechanisms of structural evolutions in semi-crystalline MBCs deformed at different temperatures to gain further insights into structure/property–function relations for mechanical properties and the shape-memory capability. As far as PCL-PIBMD is concerned, the PIBMD amorphous phase in PCL-PIBMD will be in the rubbery state if PCL-PIBMD is deformed at a temperature higher than $T_{g,\text{PIBMD}}$. Its structural response during deformation should be different from the case in which the PIBMD amorphous phase is in the glassy state if PCL-PIBMD is deformed at a temperature lower than $T_{g,\text{PIBMD}}$. Such difference is anticipated to cause distinct SMEs as well as the variation in the relative contributions of PIBMD amorphous phase and PCL crystals to switching domains.

In this work, the structural variations of PCL-PIBMD (with a 50 wt% PIBMD) deformed to a strain of 200% at $T_{\text{deform}} = 20$ or 50°C , which are below and above $T_{g,\text{PIBMD}}$, were studied by means of differential scanning calorimetry (DSC), atomic force microscopy (AFM), wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS). The corresponding shape-memory properties were evaluated via cyclic, thermomechanical tensile testing. Furthermore, a new method of toluene vapor treatment was applied in order to separate the relative contributions of PCL crystalline phase and PIBMD amorphous phase to switching domains.

2. Experimental

2.1. Materials

PCL-diol with number average molecular weight (M_n) of $2700\text{ g}\cdot\text{mol}^{-1}$ and a polydispersity of 1.7 was obtained from Solvay Caprolactones (Warrington, UK). PIBMD-diol with a number averaged molecular weight $M_n = 9300\text{ g}\cdot\text{mol}^{-1}$ was prepared by ring

open polymerization of morpholine-2,5-diones in the melt using $\text{Sn}(\text{Oct})_2$ as catalyst according to Ref. [6]. Other reagents, such as 2,2(4),4-trimethyl-hexamethylene diisocyanate, (TMDI, Aldrich, Taufkirchen, Germany), amino acids (Aldrich, Taufkirchen, Germany) and solvents (Merck, Darmstadt, Germany) were of commercial grade and used without further purification.

As reported in Ref. [6], for synthesis of PCL-PIBMD containing 50 wt% PIBMD, 24.0 g PCL-diol was reacted with 22.5 g PIBMD-diol and 3.32 mL TMDI in 110 mL *N*-methylpyrrolidone at 80°C for 24 h by using 43 μL dibutyltin dilaurate as catalyst. Subsequently, another 100 μL TMDI was added to the mixture to react for another 24 h. After reaction, the mixture was diluted with 200 mL 1,2-dichloroethane and precipitated in a tenfold excess of diethyl ether. The product was collected by suction filtration and dried in a vacuum at room temperature for 24 h. The M_n of the PCL-PIBMD product was $53\,000\text{ g}\cdot\text{mol}^{-1}$ with polydispersity of 2.0, determined by gel permeation chromatography (GPC).

2.2. Film preparation

PCL-PIBMD (2.28 g) was dissolved in chloroform (50 mL) overnight at ambient temperature. The solution casting was carried out in glass petri dishes (diameter = 80 mm, Duran Group, Wertheim, Germany) with subsequent evaporation of chloroform for 5 days. The resulting film thickness was $270\pm 30\text{ }\mu\text{m}$, measured using a thickness gauge (Hans Schmidt, Waldkraiburg, Germany).

2.3. Characterization methods

2.3.1. Gel permeation chromatography (GPC)

Multidetector GPC measurements were performed using chloroform as eluent with a flow rate of $1\text{ mL}\cdot\text{min}^{-1}$ and 0.2 wt% toluene as internal standard at 35°C . The system was equipped with a precolumn, two $300\text{ mm}\times 8.0\text{ mm}$ linear M columns (Polymer Standards Service GmbH, (PSS) Mainz, Germany) an isocratic pump 2080 and an automatic injector AS 2050 (both Jasco, Tokyo, Japan). Three detectors were used: a UV detector UV-1575 (Jasco, 275 nm); a RI detector Shodex RI-101 (Showa Denko, Japan) and the viscometer SEC-3010 (WGE, Dr. Bures, Dallgow, Germany) which were combined by a split. The molecular weights were determined using a universal calibration with polystyrene standards with M_n between $580\text{ g}\cdot\text{mol}^{-1}$ and

975 000 g·mol⁻¹ (PSS) and with the help of the SEC software WINGPC Unity (PSS).

2.3.2. Atomic force microscopy (AFM)

The morphologies of solution cast films before and after deformation at different T_{deform} s were investigated by AFM (Multimode with NanoScope V Controller, Veeco Instruments Inc.) with a temperature controller (Veeco Thermal Application Controller). The typical scan rate was 0.8–1.0 Hz. The silicon cantilevers (OLYMPUS OMCL AC200TS-R3), having a driving frequency of around 150 KHz and a spring constant of 9 N·m⁻¹, were used for measurements. The tip has a radius of 7 nm and its back and side angles are 35° and 18°, respectively.

2.3.3. Differential scanning calorimetry (DSC)

DSC experiments were conducted on a Netzsch DSC 204 Phoenix (Selb, Germany) at a heating rate of 10°C·min⁻¹ in sealed aluminum pans. The polymer samples were cooled down from room temperature to 0°C before they were heated to 200°C, while the T_m and related melting enthalpies (ΔH) were determined from DSC curves. A non-deformed PCL-PIBMD sample was measured after being preconditioned by annealing at 75°C for 10 min, then cooling down to 50°C and keeping for 10 min at T_{deform} , and afterwards cooling to 0°C with a cooling rate of 5°C·min⁻¹ by using DSC to simulate the main thermal treatment applied during programming. The deformed samples were prepared as described in the following section 2.3.4.

2.3.4. Cyclic, thermomechanical tensile tests

Cyclic, thermomechanical, tensile tests were performed on a tensile tester (Zwick Z1.0, Ulm, Germany) equipped with a thermo chamber and a temperature controller (Eurotherm Regler, Limburg, Germany). Each cycle consisted of a shape-memory creation procedure (SMCP) and recovery modules, which can be performed under two different conditions: stress-free or constant-strain. The cycles were repeated three times per test.

Programming (SMCP) was performed using test specimens which were cut from the solution cast films according to the type DIN EN ISO 527-2/1BB (length = 20 mm, width = 2 mm). The specimen was heated up from room temperature to the upper working temperature ($T_{\text{high}} = 75^\circ\text{C}$). After 10 min, the temperature was reduced to $T_{\text{deform}} = 50$ or 20°C at

5°C·min⁻¹. After another 5 min, the specimen was deformed to the strain of $\varepsilon_m = 200\%$ at a deformation speed of 1 mm·min⁻¹. Subsequently, the deformed specimen was kept at T_{deform} for 5 min to allow relaxation. Then, the specimen was cooled down to lower temperature ($T_{\text{low}} = 0^\circ\text{C}$) under constant-strain condition and equilibrated for 10 min. Finally, the stress was removed and the temporary fixed elongation temporary strain (ε_u) was determined.

Recovery under stress-free condition was induced by heating the programmed sample from 0 to 75°C at 2°C·min⁻¹ under stress-free condition. The switching temperature (T_{sw}) and recovery strain (ε_p) were determined.

Recovery under constant-strain condition was carried out after completion of the programming module by increasing the temperature from 0 to 75°C at 2°C·min⁻¹. σ_{max} and its corresponding temperature ($T_{\sigma, \text{max}}$) were determined at the maximum value of σ in the stress-temperature curve. The stress was completely released after reaching T_{high} to allow the sample recovery. The characteristics for quantification of SME, R_f and shape recovery ratio (R_r), can be calculated by Equations (1) and (2) [1]:

$$R_f = \frac{\varepsilon_u(N)}{\varepsilon_m} \quad (1)$$

$$R_r = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N-1)} \quad (2)$$

where N is the present N^{th} cycle of cyclic test.

2.3.5. Wide-angle X-ray scattering (WAXS)

WAXS measurements were performed on the Bruker D8 Discover X-ray diffraction system with a two-dimensional detector from Bruker AXS (Karlsruhe, Germany). The X-ray generator was operated at 40 kV and 40 mA on a copper-anode. The collimator was chosen 0.8 mm (beam size). The two-dimensional detector (Hi-Star) was operated in 1024×1024 pixel mode. The distance sample-detector was 150 mm and the wavelength $\lambda = 0.15418$ nm. The detector was positioned at an angular position $2\theta = 25^\circ$ in order to cover an angular range from $2\theta = 7.2$ to 43.5° . Exposure time was 120 s per scattering pattern. The raw patterns (two-dimensional) were all isotropic, thus a one-dimensional curve contains the same information as the 2D-pattern. Then an integration over an angle $\chi = 120^\circ$ and the whole 2θ -range was performed in order to obtain 1D-scatter-

ing curves using 5-point normalized binning. Non valid data points outward of the detector were not considered for integration. The scattering curves of semi-crystalline samples were decomposed into individual peaks, belonging either to the amorphous or the crystalline phase with the Bruker-software TOPAS®. A big amorphous bump was always present at $2\theta = 20^\circ$, crystalline peaks were found at various positions. The peaks of the two phases (amorphous and crystalline) were fitted with Pearson VII functions [15]. The relation of the peak position and breadth (FWHM) with the crystal size (l_c) is given by the Sherrer equation (Equation (3), parameter $k = 0.9$) [15]:

$$l_c = \frac{k \cdot \lambda}{B \cdot \cos \theta} \quad (3)$$

where B = FWHM (in radians); θ = half scattering angle; λ = wavelength of X-rays.

A custom built tensile device was used for uniaxial deformation using type ISO 527-2/1BB dumbbell test bars ($20 \times 2 \times 1$ mm) at a cross-head speed of $1 \text{ mm} \cdot \text{min}^{-1}$. Heating was provided by a heating gun (heating rate $\sim 10^\circ\text{C} \cdot \text{min}^{-1}$, non-linear), whereby cooling was enabled by a cooled Nitrogen flux (Cooling rate $\sim 10^\circ\text{C} \cdot \text{min}^{-1}$, non-linear). The temperature was monitored by a thermocouple touching the sample. For *in situ* WAXS measurements, the test specimens were fixed in the custom build tensile device. The sample was deformed to 200% strain at T_{deform} after annealing at 75°C for 10 min, and then cooled down to 0°C and kept for 10 min, which was the same procedure as in SMCP. WAXS patterns were collected at each programming stage.

2.3.6. Small-angle X-ray scattering (SAXS)

SAXS was performed on a Bruker Nanostar diffractometer (Bruker AXS, Karlsruhe, Germany), operating 40 kV and 35 mA on a copper anode. Point focussed X-rays were monochromated and parallelized by Montel-optics and collimated by a 750/400/1000 μm 3-pinhole combination, thus a 400 μm beam having a wavelength of 0.15418 nm ($\text{CuK}\alpha$) was obtained. The distance sample to the detector was 1070 mm calibrated with Silver behenate standard. A Vantec-2000 detector (2048×2048 pixel, 68 μm pixel size) was employed to record scattered intensities, the primary beam was stopped (6 mm lead beam-stop) close before the detector. The primary and secondary beam paths as well as the sample chamber

were operated under vacuum ($\sim 10^{-3}$ mbar). Samples were placed into a small powder-sample holder (0.2 mm thickness) and exposed 1 h to obtain a two dimensional scattering pattern which was corrected for spatial distortion and background subtracted (weighted with sample transmission). Isotropic scattering patterns were integrated (azimuthal average over 360°) by 5-point binning with a 0.001° (2θ) step size from $2\theta = 0.1$ to 3.2° leading into one-dimensional scattering curves of scattered intensity vs. scattering angle (I vs. 2θ). Anisotropic scattering patterns were integrated over a 10° wide azimuthal range along the axis of symmetry (fiber axis, s_3) Furthermore scattering angle was converted into scattering vector s , being $|s| = s = (2/\lambda) \sin \theta$ and a Kratky-plot (Lorenz correction $I s^2$ vs. s) was utilized to extract the long period L from the position of the peak maxima as $L = s^{-1}$ [16].

2.3.7. Toluene vapor treatment

The deformed specimens were treated in a vacuum desiccator which was first evacuated and then filled with saturated toluene vapor for 45 min. The lengths of deformed specimens after treatment, $l_{r,\text{toluene}}$, were recorded to calculate the partial recovery ratio in toluene, $R_{r,\text{toluene}}$, by Equation (4). After toluene vapor treatment, the sample was heated to 75°C to allow for complete recovery. The final recovery ratio after heating, $R_{r,\text{heating}}$, was calculated using the lengths of the sample after heating, $l_{r,\text{heating}}$ according to Equation (5). The content of toluene which was absorbed in the specimens was 8.0%, which was detected by GPC.

$$R_{r,\text{toluene}} = \frac{l_e - l_{r,\text{toluene}}}{l_e - l_0} \quad (4)$$

$$R_{r,\text{heating}} = \frac{l_e - l_{r,\text{heating}}}{l_e - l_0} \quad (5)$$

where l_0 is the original length of sample and l_e is the deformed length of sample.

The content of toluene, which was absorbed in the vapor treated PCL-PIBMD test specimens, was quantified by chromatography experiments using the GPC equipment described in 2.3.1. A series of DMF/toluene mixtures with varying toluene concentration ranging from 0.02 to 10 wt% were analyzed with the GPC system for creation of a calibration curve. 0.1 g pieces were cut from the middle of the deformed specimens after toluene vapor treatment and then

dissolved in DMF resulting in a 0.2 wt% concentration and then investigated with the GPC system. The obtained toluene signal was evaluated by using the standard calibration curve.

3. Results and discussion

3.1. Thermal properties

The thermal properties of deformed PCL-PIBMD films were examined using DSC and compared to that obtained for a preconditioned non-deformed sample (see paragraph 2.3.3). As shown in Figure 1, only a PIBMD melting peak at 168°C can be observed in the non-deformed PIBMD sample. The reason might be that the existing PIBMD crystalline domains highly restricted the crystallization of PCL domains during the preconditioning procedure when cooled from 75 to 0°C with a cooling rate of 5°C·min⁻¹. Therefore, before deformation at 20 or 50°C, only PIBMD crystals existed in PCL-PIBMD, while all PCL domains were in the amorphous state. The PIBMD amorphous phase with a $T_{g,PIBMD} \approx 42^\circ\text{C}$ is in the glassy state at 20°C or in the rubbery state at 50°C. After deformation at 20 or 50°C, both PCL and PIBMD melting peaks were observed in the heating scan, demonstrating that the generation of oriented PCL chains during deformation facilitated the crystallization of PCL domains. A magnified view

of the PCL melting peaks is shown in Figure 1b. A pronounced PCL melting peak in the range from 26 to 45°C with $\Delta H_{m,PCL} = 27 \text{ J}\cdot\text{g}^{-1}$ was obtained for the sample deformed at 20°C, while deformation at 50°C resulted in a broad endothermic peak ranging from 27 to 54°C, having a slightly higher $\Delta H_{m,PCL}$ of 29 J·g⁻¹. The difference in the melting temperature interval indicates that PCL crystals with a higher crystal thickness exist only in samples deformed at 50°C. As shown in Table 1, the melting enthalpies of PCL domains in the sample deformed at 50°C were higher than the sample deformed at 20°C, suggesting a higher degree of crystallinity of PCL domains after deformation at a higher T_{deform} . The variation of T_{deform} did not significantly influence the melting enthalpy of the PIBMD crystals (27~29 J·g⁻¹). Compared to the non-deformed samples with a PIBMD melting enthalpy of 22 J·g⁻¹, it can be anticipated that strain-induced crystallization was responsible for the observed increase in crystallinity when the samples were deformed to 200%.

3.2. Surface morphologies

AFM experiments were performed to visualize the surface morphologies of PCL-PIBMD samples after deformation at various temperatures, as presented in Figure 2. Polymer crystals as typical spherulites,

Table 1. Thermal properties of deformed and non-deformed PCL-PIBMD solution cast films calculated from DSC measurements

T_{deform} [°C]	$T_{m,PCL}$ [°C]	$\Delta H_{m,PCL}$ [J·g ⁻¹]	$T_{m,PIBMD}$ [°C]	$\Delta H_{m,PIBMD}$ [J·g ⁻¹]
Non-programmed	–	–	168	22
20	40	21	168	27
50	41	29	170	29

Note: the estimated error for T is $\pm 1^\circ\text{C}$, for ΔH is $\pm 2 \text{ J}\cdot\text{g}^{-1}$.

Figure 1. DSC heating curves of (a) deformed and non-deformed PCL-PIBMD solution cast films and (b) magnified view of PCL crystals melting peaks

Figure 2. AFM phase images (a, b, c) and height images (d, e, f) of PCL-PIBMD films before (a, d) and after deformation to 200% strain at 50°C (b, e) and 20°C (c, f). The deformation direction was vertical

which are composed of highly ordered edge-on lamellae, were observed in the non-deformed sample as shown in Figures 2a and 2d. The large spherulites did not change evidently when increasing the temperature from 20 to 60°C (not presented here), indicating that those crystals originated from PIBMD domains. These results matched with the DSC data. It can also be observed that PIBMD crystals are enriched on the top surface of solution cast film. Further investigations with the spin coated PCL-PIBMD films (data not shown here) demonstrated that that PCL segments were preferentially enriched on the top layer in the molten state, indicating a smaller surface energy of PCL compared to PIBMD. The newly formed PIBMD crystals broke out the ordered phase separated morphology and fully wetted the free surface, while the crystallization of PCL domains was confined in the PIBMD lamellae, forming fractionated crystals. Thus, only large PIBMD spherulites can be observed on the topography of PCL-PIBMD films. More importantly, compared to the initial morphology without deformation, it can be illustrated from AFM phase images that the PIBMD spherulites were deformed along the deformation direction, as shown in Figures 2b–2c and 2e–2f. In addition, higher levels of structural orientations of PIBMD crystals can be observed if PCL-PIBMD film was deformed at 50°C.

3.3. Crystalline structures

For exploring the nanostructural changes during the deformation of PCL-PIBMD samples *in-situ* 2D WAXS patterns were recorded at different temperatures, which are displayed in Figure 3a. At 50°C, a strong reflection as an inner bright ring ($2\theta = 8.8^\circ$) was identified with several other weak reflections as shown in Figures 3a (I and IV), all of which belong to the PIBMD crystals. Isotropic scattering indicated that randomly distributed PIBMD lamellae did not present evident orientation before deformation. With stretching to 200% at 50°C (Figure 3a II), an equatorial scattering maximum appeared at the inner ring ($2\theta = 8.8^\circ$) of PIBMD crystal reflections as indicated by the arrow, illustrating the orientation of PIBMD crystals perpendicular to the deformation direction. The deformed sample was then cooled to 0°C (Figure 3a III) while the deformation was fixed. The ring of (110) reflection ($2\theta = 21.3^\circ$) showed a strong equatorial scattering maximum, which suggested the generation of PCL crystals perpendicular to the deforming direction. For the sample deformed at 20°C (Figure 3a V), the equatorial (110) scattering maximum confirmed that the PCL crystals appeared only after stretching at 20°C (highlighted by an arrow). This indicates that the strain-induced crystallization of PCL domains

occurred during the stretching and the newly generated PCL crystals aligned perpendicular to the deformation direction. Usually, crystals generated by strain-induced crystallization exhibit highly ordered structures compared to that formed by thermal-induced crystallization during cooling. This conclusion could be confirmed by the DSC results, where a broad PCL melting peak was obtained for the sample deformed at 50°C and a smaller pronounced melting peak when programmed at 20°C.

No difference in the nanostructure was observed when the samples were further cooled to 0°C (Figure 3a VI). The size of PIBMD crystals ($l_{c, \text{PIBMD}}$) after deformation was calculated and shown in Table 2. Compared to the non-deformed sample, the size of PIBMD crystals decreased from 16.4 to 15.8–15.9 nm after deformation at 50 or 20°C. These results suggested that the fragmentation of PIBMD crystals occurred during deformation and its level

was similar when PCL-PIBMD was deformed to 200% at 50 or 20°C.

For quantification of the resulting degree of orientation of the crystalline structures, the corresponding azimuthal scans of the WAXS patterns were analyzed. Here, the intensity distribution of the ring (110) ($2\theta = 21.3^\circ$) from the PCL crystal reflections were explored at each deformation stage as shown in Figure 3c and 3d, which was corresponding to the SMCP. The full width at half maximum (FWHM) of crystal structures were listed in Table 2. Before deformation, no peaks can be found in the profiles, indicating that no PCL crystals existed in the non-deformed samples. In the azimuthal profiles obtained after deformation at 50°C also no PCL crystals are present, while after cooling to 0°C a pronounced increase in orientation was obtained ($\text{FWHM}_{\text{PCL}} = 25.7^\circ$) caused by newly generated PCL crystals. In contrast, the azimuthal profiles of the sample

Figure 3. WAXS (a) and SAXS (b) patterns of PCL-PIBMD films (I, IV) before and (II, V) after deformation to 200% strain at (I, II) 50°C and (IV, V) 20°C and cooled to (III, VI) 0°C, respectively. Intensity distribution of (a) the ring (110) ($2\theta = 21.3^\circ$) from PCL crystal reflections from WAXS patterns when samples were deformed at (c) 20°C and (d) 50°C. The deformation direction was vertical

deformed at 20°C ($\text{FWHM}_{\text{PCL}} = 33.3^\circ$) and fixed at 0°C ($\text{FWHM}_{\text{PCL}} = 32.3^\circ$), were found to be almost identical (see Figure 3c), indicating that a lower degree of orientation of PCL crystals is achieved by deformation at 20°C. In addition, the azimuthal analysis of the PIBMD crystal structure was performed (Figure 3d). Here a higher degree of orientation could be obtained when the samples were deformed at 50°C compared to the deformation at 20°C. This result is in good agreement with the interpretation of the AFM analysis.

During programming at 50°C the overall applied deformation can be solely fixed by the PIBMD crystals existing at 50°C, whereby the oriented amorphous PCL domains can crystallize in the subsequent cooling to 0°C. On the contrary, a difference is given when deforming the multiblock copolymer at 20°C. Here the PCL domains form strain-induced crystals during the deformation process. Thus, the deformability of the amorphous PCL domains would be additionally restricted by newly formed PCL crystals and glassy PIBMD domains. Therefore, a decrease in degree of orientation of PCL and PIBMD chains represented by lower FWHM values is caused. As the PCL domains exhibit a low glass transition temperature around -60°C , it can be assumed that the relaxation of the rubbery PCL chains at 20 or 50°C is almost similar, but that the chain deformability (which is higher at 50°C) is predominantly controlling the achievable degree of orientation after programming.

The changes in the lamellar structure during deformation can be extracted directly from the *in-situ* 2D SAXS patterns. As shown in Figures 3b (I and IV), before deformation, the SAXS patterns exhibited single isotropic scattering related to the stacks of randomly oriented chain-folded PIBMD lamellae at 50°C, suggesting that no preferred orientation existed in non-deformed samples. After deformation up to a strain of 200% at 50°C (Figure 3b II), the pattern

became oblate, indicating the scattering maximum along the meridional direction (parallel to deformation direction) shifted to a lower angle, whereas the scattering maximum in equatorial direction (vertical to deformation direction) moved to a higher value. Followed by deforming at 50°C, samples were cooled to 0°C to fix the temporary shape (Figure 3b III). Two scattering maxima appeared in meridian, suggesting the generation of PCL crystalline lamellae during cooling, which were oriented perpendicular to the deformation direction. For the PCL-PIBMD sample stretched at 20°C to 200% (Figure 3b V), two strong scattering maxima were clearly visible along the meridional direction, which further prove that the strain-induced PCL crystals were vertical to the deformation direction during stretching. After fixing the temporary shape at 0°C (Figure 3b VI), no evident changes can be observed compared to the deformed sample at 20°C. The shift of the scattering maximum in SAXS patterns was related to the changes in the long period (L), which are summarized in Table 2. The long period in meridional direction (L_{mer}) increased from 13.3 to 13.5 nm while the long period in equator (L_{equ}) was reduced from 13.3 to 10.5 nm after deformation to 200% at 50°C. It can be considered that the deformation enlarged the average spacing between the lamellae aligned perpendicularly to the deformation direction leading to the increase in L_{mer} , while the space between the lamellae which are parallel to the deformation direction decreased. After cooling to 0°C, the reductions in both L_{mer} and L_{equ} were observed. The reason could be the generation of small PCL crystals among the PIBMD lamellae. When the sample was deformed at 20°C, the L_{equ} decreased to 9.9 nm, while L_{mer} turned to 11.1 nm. The reduction in both L_{mer} and L_{equ} at 20°C suggested that the crystal structures generated during stretching resulted from strain-induced crystallization of PCL domains. Only a slight difference can be observed when the sample was cooled

Table 2. Thermal properties and crystal structures obtained or calculated from DSC, WAXS and SAXS measurements

T_{deform} [°C]	T [°C]	L_{equ} [nm]	L_{mer} [nm]	$l_{\text{c, PIBMD}}$ [nm]	$\text{FWHM}_{\text{PIBMD}}$ [°]	FWHM_{PCL} [°]
Non-programmed	20	13.0	13.0	16.4	–	–
Non-programmed	50	13.3	13.3	16.4	–	–
50	50	10.5	13.5	15.8	64.3	–
50	0	9.0	12.8	15.9	62.9	25.7
20	20	9.9	11.1	15.9	85.8	33.3
20	0	8.9	10.9	15.8	84.3	32.3

Note: L_{equ} and L_{mer} were calculated from SAXS results and $l_{\text{c, PIBMD}}$ was calculated from WAXS data. The estimated error for L and l_{c} are ± 0.2 nm and for FWHM is 0.7° .

down to 0°C after deformation since T_{deform} was already lower than $T_{\text{g, PIBMD}}$ and $T_{\text{m, PCL}}$. The SAXS results fully agreed with the WAXS results.

3.4. Shape-memory properties

The shape-memory properties of solution cast PCL-PIBMD films performed at two T_{deform} s were measured by cyclic, thermomechanical tensile tests. The stress-temperature-strain curves of the first cycle are shown in Figure 4. In SMCP, the PCL-PIBMD specimens were stretched to a strain of ε_{m} of 200% at a deformation rate of $1 \text{ mm} \cdot \text{min}^{-1}$. The T_{deform} s were chosen as 50 and 20°C, respectively, which was above or below both $T_{\text{m, PCL}}$ and $T_{\text{g, PIBMD}}$. The deformed shapes were fixed when the temperature was decreased to T_{low} of 0°C. Finally, by heating the samples to 75°C under stress-free or constant-strain conditions the recovery was initiated.

Table 3 lists the shape-memory properties determined for the PCL-PIBMD samples programmed at different T_{deform} s. Excellent values for R_{f} above 92% as well as R_{r} around 90% in the first cycle and $R_{\text{r}} \approx 99\%$ in the 2nd and 3rd cycle were reached for both samples. The T_{sw} decreased from 44 to around 39°C as well as the temperature where the maximum recovery force occurred ($T_{\sigma, \text{max}}$) was reduced from 56 to 30°C when T_{deform} was reduced from 50 to 20°C. This effect could be caused by the different

structures of PCL crystals, as demonstrated by DSC curves, and different degree of orientation of PIBMD domains, as shown in AFM images. In addition, a higher stress $\sigma(\varepsilon_{\text{m}})$ was required to achieve the same strain at 20°C since the PIBMD amorphous phase was in glassy state. In addition, the ratio of $\sigma_{\text{max}}/\sigma(\varepsilon_{\text{m}})$ decreased largely from 60.0 to 38.2% when decreasing the T_{deform} from 50 to 20°C, suggesting that more energy was dissipated during stretching for the slippage and the fragmentation of PIBMD lamellae.

3.5. Toluene vapor treatment

As demonstrated before [7], in case of PCL-PIBMD, both PIBMD amorphous phase and PCL crystalline phase can act as switching domains since they present a similar T_{trans} . Therefore, the temporary shape of deformed samples can be fixed by the crystallization of PCL domains and the vitrification of amorphous PIBMD phase. Since toluene is a good solvent for PCL but a poor solvent for PIBMD, it can be used to trigger the partial recovery of deformed specimens by selectively eliminating PCL crystals by the solvation of PCL segments. In addition, since PIBMD amorphous phases still stayed in the glassy state at room temperature after the treatment with toluene vapor (determined by DMTA, not shown here), the temporary shape which is fixed by vitrification of PIBMD amorphous phase cannot recover

Table 3. Shape-memory properties for PCL-PIBMD films programmed to 200% at 50 and 20°C, respectively, with the strain rate of $1 \text{ mm} \cdot \text{min}^{-1}$

T_{deform} [°C]	$R_{\text{f}(1)}$ [%]	$R_{\text{r}(1)}$ [%]	$R_{\text{f}(2,3)}$ [%]	$R_{\text{r}(2,3)}$ [%]	T_{sw} [°C]	$\sigma(\varepsilon_{\text{m}})$ [MPa]	σ_{max} [MPa]	$\sigma_{\text{max}}/\sigma(\varepsilon_{\text{m}})$ [%]	$T_{\sigma, \text{max}}$ [°C]
50	96	90	96	99	44	12.4	7.4	60.0	56
20	94	90	92	99	39	25.1	9.6	38.2	30

Note: The $R_{\text{f}(1)}$, $R_{\text{r}(1)}$, T_{sw} , were determined from the 1st cycle measurement under stress-free recovery; $R_{\text{f}(2,3)}$ and $R_{\text{r}(2,3)}$ were the average values of the 2nd and 3rd cycle measurement under stress-free recovery; $\sigma(\varepsilon_{\text{m}})$, σ_{max} , $\sigma_{\text{max}}/\sigma(\varepsilon_{\text{m}})$ and $T_{\sigma, \text{max}}$ were determined from the 1st cycle measurement under constant-strain recovery. $R_{\text{r, toluene}}$ was measured using a centimeter ruler. The estimated errors for R_{f} and R_{r} is $\pm 2\%$, for T is $\pm 2^\circ\text{C}$, for σ is $\pm 0.5 \text{ MPa}$ and for $R_{\text{r, toluene}}$ is $\pm 4\%$.

Figure 4. The first cycle curves of cyclic tests of PCL-PIBMD films programmed to 200% at 50 and 20°C, respectively, with the strain rate of $1 \text{ mm} \cdot \text{min}^{-1}$ and recovered under (a) stress-free and (b) constant-strain conditions

considerably. Thus, after placing the deformed specimens in toluene vapor for 45 min at room temperature, the contributions of $T_{g, \text{PIBMD}}$ and $T_{m, \text{PCL}}$ to the SME switching domains can be distinguished.

Figure 5 presents the photographic pictures of deformed samples before and after toluene vapor treatment and after reheating to 75°C in comparison to a non-deformed sample. It can be observed that the lengths of deformed specimens decreased after 45 min, indicating a partial recovery. DSC measurements were performed to examine the thermal properties of treated samples (not shown here). After toluene vapor treatment, the melting peaks of PCL domains disappeared, suggesting that the PCL crystals were dissolved by vapor toluene. The orientated PCL chains which were fixed by PCL crystals, thus fully recovered driven by increasing the entropy. The PIBMD crystals, however, did not vary considerably during the treatment, demonstrating that (1) the net-points, or the ability to keep the permanent shape of PCL-PIBMD samples, were not influenced by toluene, and more importantly, (2) the variation in PIBMD amorphous phase could be neglected. Then these samples after the treatment in toluene vapor were reheated to 75°C, where the orientated chains fixed by vitrification of PIBMD domains were allowed to recover. A second recovery process can be observed and the lengths of deformed samples further reduced. As declared in Table 4, the total recovery ratios after heating, $R_{r, \text{heating}}$, for samples deformed at 50 and 20°C were comparable with the recovery ratios measured from cyclic, thermomechanical tensile tests. Therefore, the recovery ratio after toluene vapor treatment ($R_{r, \text{toluene}}$) can be con-

Table 4. The recovery ratio after toluene vapor treatment and heating procedure for PCL-PIBMD films programmed to 200% at 50 and 20°C, respectively, with the strain rate of 1 mm·min⁻¹

T_{deform} [°C]	$R_{r, \text{toluene}}$ [%]	$R_{r, \text{heating}}$ [%]	$R_{r, \text{toluene}}/R_{r, \text{heating}}$ [%]
50	73	88	82.9
20	87	90	96.7

Note: $R_{r, \text{toluene}}$ and $R_{r, \text{heating}}$ were measured using a centimeter ruler after toluene vapor treatment and heating to 75°C, respectively. The estimated errors for $R_{r, \text{toluene}}$ and $R_{r, \text{heating}}$ are $\pm 2\%$.

sidered as the absolute recovery ratio resulting from PCL crystals as the switching domains, while the ratio of $R_{r, \text{toluene}}/R_{r, \text{heating}}$ can be defined as the relative contribution of PCL crystals to the total recovery of deformed PCL-PIBMD specimens. Table 4 shows that the $R_{r, \text{toluene}}$ value of samples deformed at 20°C was larger than that deformed at 50°C, while the $R_{r, \text{toluene}}/R_{r, \text{heating}}$ increased from 82.9 to 96.7% when T_{deform} changed from 50 to 20°C. These results indicated that the temporary shape of the samples deformed at 20°C was almost totally fixed by the strain-induced crystallization of PCL domains. Based on all the obtained data and results, the mechanisms of structural variations of PCL-PIBMD specimens programmed to 200% strain at 50 and 20°C are discussed in the following. In the semi-crystalline MBC of PCL-PIBMD, PCL amorphous domains, PIBMD amorphous domains, and PIBMD crystalline domains existed before deformation. The uniaxial deformation at 50°C first resulted in the orientation of PIBMD and PCL amorphous phases. With increasing the strain, the stress was transferred from orientated amorphous chains to PIBMD crystals, leading to their fragmentation.

Figure 5. Photos of deformed PCL-PIBMD samples (a) after deformation, (b) after toluene vapor treatment and (c) after heating to 75°C in comparison to a non-deformed sample as a reference. For the deformed films, the strain was 200% with the strain rate of 1 mm·min⁻¹ and the deformation temperatures were 50 and 20°C, respectively.

At 50°C, strain-induced crystallization of PCL domains was negligible, since the temperature was higher than $T_{m,PCL}$. Only thermally-induced crystallization of PCL domains occurred during the subsequent cooling process, in which the entangled polymer chains preferred to form crystals with chain-folded conformation. However, at 20°C uniform chain-extended crystal structures were generated because of strain-induced crystallization. A lower $T_{m,PCL}$ and its narrower range, thus, were achieved, correspondingly decreasing T_{sw} and $T_{\sigma,max}$. The amorphous PIBMD phase stayed in rubbery or glassy state at 50 or 20°C, respectively. When the sample was deformed at 50°C, both PCL and PIBMD amorphous phases can be oriented. After cooling down the temperature to 0°C, the oriented PIBMD amorphous phase was fixed by its vitrification. Therefore, both PCL crystals and PIBMD amorphous phase can contribute to the fixation of the temporary shape.

When the PCL-PIBMD samples were programmed at 20°C, however, the PIBMD amorphous phase was in the glassy state. Therefore, the chain orientation was mainly restricted to PCL amorphous phase and the temporary shape was fixed mainly by the crystallization of PCL domains. For the same reason, a higher stress was required for deforming the sample and more energy dissipation was observed during stretching, generating the larger $\sigma(\epsilon_m)$ but smaller $\sigma_{max}/\sigma(\epsilon_m)$ at 20°C.

5. Conclusions

In PCL-PIBMD MBCs, the amorphous PIBMD domains and crystallizable PCL domains can serve as switching domains, while the PIBMD crystals act as physical netpoints determining the permanent shape. The structural evolution of PCL-PIBMD samples during deformation depended on the deformation temperature and resulted in different contributions of PCL crystals and amorphous PIBMD domains to the switching domains. When the samples were deformed at 50°C, which was above $T_{m,PCL}$ and $T_{g,PIBMD}$, both PCL and PIBMD amorphous domains were oriented. The temporary shape of deformed PCL-PIBMD, thus, was fixed by the thermally-induced chain-folded PCL crystals and vitrification of PIBMD domains, leading to their joint contribution to switching domains. However, when the samples were deformed at 20°C, which is

below $T_{m,PCL}$ and $T_{g,PIBMD}$, only PCL crystallizable domains acted as switching domains by strain-induced crystallization, since PIBMD amorphous phase was in the glassy state. In such a case a higher programming stress is required and more energy dissipation occurred during deformation when compared to $T_{deform} = 50^\circ\text{C}$. Here we could demonstrate that the results achieved by a combination of structural and thermo-mechanical investigations are useful for understanding of complicated SME mechanisms in MBCs containing two crystallizable segments. More importantly, this work offers a new method to clarify and adjust the relative contribution of crystalline and amorphous switching domains with overlapping or almost identical transition temperature ranges in such MBC.

References

- [1] Behl M., Razzaq M. Y., Lendlein A.: Multifunctional shape-memory polymers. *Advanced Materials*, **22**, 3388–3410 (2010). DOI: [10.1002/adma.200904447](https://doi.org/10.1002/adma.200904447)
- [2] Xie T.: Recent advances in polymer shape memory. *Polymer*, **52**, 4985–5000 (2011). DOI: [10.1016/j.polymer.2011.08.003](https://doi.org/10.1016/j.polymer.2011.08.003)
- [3] Karger-Kocsis J., Kéki S.: Biodegradable polyester-based shape memory polymers: Concepts of (supra) molecular architecturing. *Express Polymer Letters*, **8**, 397–412 (2014). DOI: [10.3144/expresspolymlett.2014.44](https://doi.org/10.3144/expresspolymlett.2014.44)
- [4] Kolesov I. S., Radusch H.-J.: Multiple shape-memory behavior and thermal-mechanical properties of peroxide cross-linked blends of linear and short-chain branched polyethylenes. *Express Polymer Letters*, **2**, 461–473 (2008). DOI: [10.3144/expresspolymlett.2008.56](https://doi.org/10.3144/expresspolymlett.2008.56)
- [5] Kang S. M., Lee S. J., Kim B. K.: Shape memory polyurethane foams. *Express Polymer Letters*, **6**, 63–69 (2012). DOI: [10.3144/expresspolymlett.2012.7](https://doi.org/10.3144/expresspolymlett.2012.7)
- [6] Feng Y., Guo J.: Biodegradable polydepsipeptides. *International Journal of Molecular Sciences*, **10**, 589–615 (2009). DOI: [10.3390/ijms10020589](https://doi.org/10.3390/ijms10020589)
- [7] Feng Y., Behl M., Kelch S., Lendlein A.: Biodegradable multiblock copolymers based on oligodepsipeptides with shape-memory properties. *Macromolecular Bioscience*, **9**, 45–54 (2009). DOI: [10.1002/mabi.200800199](https://doi.org/10.1002/mabi.200800199)
- [8] Feng Y., Lu J., Behl M., Lendlein A.: Degradable depsipeptide-based multiblock copolymers with polyester or polyetherester segments. *The International Journal of Artificial Organs*, **34**, 103–109 (2011). DOI: [10.5301/IJAO.2011.6402](https://doi.org/10.5301/IJAO.2011.6402)

- [9] Bao R., Ding Z., Zhong G., Yang W., Xie B., Yang M.: Deformation-induced morphology evolution during uniaxial stretching of isotactic polypropylene: Effect of temperature. *Colloid and Polymer Science*, **290**, 261–274 (2012).
DOI: [10.1007/s00396-011-2550-5](https://doi.org/10.1007/s00396-011-2550-5)
- [10] Jiang Z., Tang Y., Men Y., Enderle H-F., Lilge D., Roth S. V., Gehrke R., Rieger J.: Structural evolution of tensile-deformed high-density polyethylene during annealing: Scanning synchrotron small-angle X-ray scattering study. *Macromolecules*, **40**, 7263–7269 (2007).
DOI: [10.1021/ma0627572](https://doi.org/10.1021/ma0627572)
- [11] Sarva S. S., Hsieh A. J.: The effect of microstructure on the rate-dependent stress–strain behavior of poly(urethane urea) elastomers. *Polymer*, **50**, 3007–3015 (2009).
DOI: [10.1016/j.polymer.2009.04.025](https://doi.org/10.1016/j.polymer.2009.04.025)
- [12] Hu J. L., Ji F. L., Wong Y. W.: Dependency of the shape memory properties of a polyurethane upon thermomechanical cyclic conditions. *Polymer International*, **54**, 600–605 (2005).
DOI: [10.1002/pi.1745](https://doi.org/10.1002/pi.1745)
- [13] McClung A. J., Tandon G. P., Baur J. W.: Strain rate- and temperature-dependent tensile properties of an epoxy-based, thermosetting, shape memory polymer (Veriflex-E). *Mechanics of Time-Dependent Materials*, **16**, 205–221 (2012).
DOI: [10.1007/s11043-011-9148-7](https://doi.org/10.1007/s11043-011-9148-7)
- [14] Azra C., Plummer C. J. G., Månson J-A. E.: Isothermal recovery rates in shape memory polyurethanes. *Smart Materials and Structures*, **20**, 082002/1–082002/10 (2011).
DOI: [10.1088/0964-1726/20/8/082002](https://doi.org/10.1088/0964-1726/20/8/082002)
- [15] Scherrer P.: Bestimmung der inneren Struktur und der Größe von Kolloidteilchen mittels Röntgenstrahlen. in ‘*Kolloidchemie Ein Lehrbuch*’ (Ed.: Zsigmondy R.) Springer, Berlin, 387–409 (1912).
DOI: [10.1007/978-3-662-33915-2_7](https://doi.org/10.1007/978-3-662-33915-2_7)
- [16] Stribeck N.: X-ray scattering of soft matter. Springer, Berlin (2007).