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# Hydrolytic Degradation of Actuators Based on Copolymer Networks From Oligo( $\epsilon$ -caprolactone) Dimethacrylate and *n*-Butyl Acrylate

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## ABSTRACT

Shape-memory polymer actuators often contain crystallizable polyester segments. Here, the influence of accelerated hydrolytic degradation on the actuation performance in copolymer networks based on oligo( $\epsilon$ -caprolactone) dimethacrylate (OCL) and *n*-butyl acrylate is studied. The semi-crystalline OCL was utilized as crosslinker with molecular weights of 2.3 and 15.2 kg·mol<sup>-1</sup> (ratio: 1:1 wt%) and *n*-butyl acrylate (25 wt% relative to OCL content) acted as softening agent creating the polymer main chain segments within the network architecture. The copolymer networks were programmed by 50% elongation and were degraded by means of alkaline hydrolysis utilizing sodium hydroxide solution (pH = 13). Experiments were performed in the range of the broad melting range of the actuators at 40 °C. The degradation of test specimen was monitored by the sample mass, which was reduced by 25 wt% within 105 d. As degradation products, fragments of OCL with molecular masses ranging from 400 to 50.000 g·mol<sup>-1</sup> could be detected by NMR spectroscopy and GPC measurements. The cleavage of ester groups included in OCL segments resulted in a decrease of the melting temperature ( $T_m$ ) related to the actuator domains (amorphous at the temperature of degradation) and simultaneously, the  $T_m$  associated to the skeleton domain was increased (semi-crystalline at the temperature of degradation). The alkaline hydrolysis decreased the polymer chain orientation of OCL domains until a random alignment of crystalline domains was obtained. This result was confirmed by cyclic thermomechanical actuation tests. The performance of directed movements decreased almost linearly as function of degradation time resulting in the loss of functionality when the orientation of polymer chains disappeared. Here, actuators were able to provide reversible movements until 91 d when the accelerated bulk degradation procedure using alkaline hydrolysis (pH = 13) was applied. Accordingly, a lifetime of more than one year can be guaranteed under physiological conditions (pH = 7.4) when, e.g., artificial muscles for biomimetic robots as potential application for these kind of shape-memory polymer actuators will be addressed.

## INTRODUCTION

Soft actuators are capable of reversible movements controlled by an external stimulus. A potential application is artificial muscles for biomimetic robots [1-4]. In contrast to liquid-crystalline elastomers [5-7], shape-memory polymer actuators provide predesignated directed movements between two stable shapes according to retained geometric information; moreover, they are reprogrammable [8-12]. In this context, reversible bidirectional shape-shifts could be realized in semi-crystalline copolymer networks, in which conformational changes within an actuation domain (semi-crystalline fraction with a low thermal transition) resulted in melt-induced contraction and crystallization-induced elongation [13, 14]. Here, the geometric information about the intended reversible macroscopic shape shift is created by a thermomechanical treatment, is stored in the skeleton domain (crystalline fraction associated to a high thermal transition), and is accurately defined by the resulting polymer chain orientation within the skeleton domain. By changing, e.g. the temperature between  $T_{low}$  (temperature below thermal transition of the actuator domain) and  $T_{sep}$  (separation temperature, between thermal transitions of actuator domain and skeleton domain) reversible macroscopic movements related to the geometric information of the skeleton domain can be obtained. This reversible macroscopic shape shift can be enabled by an actuator system multiple times, whereby up to several hundred actuation cycles were reported without losing performance [15]. As the presented polymeric actuators are often based on polyesters, hydrolysis, especially in an aqueous environment, would degrade the polymer network, which would affect directed movements.

In this work, the influence of changes within the actuator and skeleton domain induced by cleavage of ester groups on a macroscopic reversible movement is addressed. As model system copolymer networks based on oligo( $\epsilon$ -caprolactone) dimethacrylate (OCL) and *n*-butyl acrylate (BA) were selected, in which the actuation was enabled close to a physiological relevant temperature range [16]. Here, a broad melting transition was realized in OCL-BA copolymer networks as OCL segments of different molecular weights (2.3 and 15.2 kg·mol<sup>-1</sup>) were incorporated. In this case, actuator and skeleton domains were generated by crystalline phases of OCL when  $T_{sep}$  was specified within the melting range ( $T_{sep}$  ranged between 37 °C and 50 °C). For these kinds of copolymer networks, a low degradation rate with 5 wt% mass loss within 499 days was reported at 37 °C utilizing a phosphate buffer solution with a pH of 7 [17]. Accordingly, accelerated degradation conditions via alkaline hydrolysis (pH = 13) at 40 °C as  $T_{sep}$  were selected to investigate how pronounced cleavage within polymer architecture has to be until an actuator will lose performance of directed movements and consequently its functionality. In the following, we also present the characterization of cleaved products as both OCL and BA include ester moieties, we describe the influence of alkaline hydrolysis on polymer chain orientation, and the changes in thermal properties and actuation as function of degradation time.

## EXPERIMENTAL

### Materials

Oligo( $\epsilon$ -caprolactone) diol (OCL-diOH) with a number-average molecular weight of  $M_n = 2.3$  kg·mol<sup>-1</sup> was purchased from Solvay Chemicals (Warrington, UK). OCL-diOH with  $M_n = 15.8$  kg·mol<sup>-1</sup> was synthesized by ring-opening polymerization according to the procedure explained in reference [16]. The OCL-diOHs were modified with 2-isocyanatoethyl methacrylate (IEMA, Sigma-Aldrich, Taufkirchen, Germany) according to the procedure described elsewhere [18]. *N*-butyl acrylate (BA) was purified

using inhibitor-remover (both from Sigma–Aldrich, Taufkirchen, Germany). Copolymer networks based on OCL-diIEMA ( $M_n = 2.5 \text{ kg}\cdot\text{mol}^{-1}$  and  $16.0 \text{ kg}\cdot\text{mol}^{-1}$ , ratio 1:1 wt%) and BA (25 wt% in relation to OCL-IEMA) were synthesized by photo-induced copolymerization with a high-pressure mercury lamp using a F300M (Fusion UV Systems, Gaithersburg, MD) system at a light intensity around  $122 \text{ mW}\cdot\text{cm}^{-1}$  according to [16]. The obtained OCL-BA copolymer networks were extracted with chloroform for three times to remove unreacted components and were dried in vacuum until constant weight was achieved.

### Degradation experiments

Samples in their programmed shape were incubated in a sodium hydroxide solution (20 mL per sample, 0.1 M, pH = 13) at  $40 \pm 1 \text{ }^\circ\text{C}$ . At certain time intervals, samples were removed from the solution, were washed three times with distilled water to remove sodium hydroxide, were dried, and were characterized by the remaining sample mass ( $m_{re}$ ), swelling ( $Q$ ) in chloroform, nuclear magnetic resonance spectroscopy (NMR), differential scanning calorimetry (DSC), wide angle X-ray scattering (WAXS), and cyclic, thermomechanical tensile tests.

In order to investigate degradation products released in the sodium hydroxide solution, the OCL(75)BA sample was removed from the degradation solution, the degradation solution was freeze-dried, the remaining components were dissolved in chloroform, and the chloroform solution was filtered to remove sodium hydroxide (insoluble in chloroform). The obtained solution was dried under vacuum until constant weight was achieved and the degradation products were analyzed by gel permeation chromatography (GPC) and NMR. The removed OCL(75)BA sample was extracted with chloroform to investigate cleaved products, which are unable of diffuse out of the network structure. Chloroform was then dried under vacuum until constant weight was achieved and the degradation products were also analyzed by GPC and NMR.

### Characterization methods

For the determination of the remaining sample mass ( $m_{re}$ ) and the swelling in chloroform ( $Q$ ), samples were extracted with chloroform for three times and dried until constant weight was achieved. The remaining sample mass was determined by comparing the weight before and after extraction. The degree of swelling in chloroform was calculated as the ratio between the sample mass swollen in chloroform and after extraction.

$^1\text{H-NMR}$  spectra were recorded at  $25 \text{ }^\circ\text{C}$  in  $\text{CDCl}_3$  with a Bruker Avance 500 spectrometer (500 MHz, Bruker, Karlsruhe, Germany) with a relaxation time of 15 seconds for polymeric networks (after extraction with chloroform) and with 2 seconds for utilized oligomers.

DSC experiments were performed on a Netzsch DSC 204 Phoenix (Netzsch, Selb, Germany) in the temperature range between  $-100 \text{ }^\circ\text{C}$  and  $100 \text{ }^\circ\text{C}$  with heating and cooling rates of  $10 \text{ K}\cdot\text{min}^{-1}$  in sealed aluminium pans.

WAXS measurements were conducted at ambient temperature in transmission geometry utilizing X-ray diffraction system Bruker D8 Discover (generator operated at 40 kV and 40 mA) with a two-dimensional detector from Bruker AXS (Karlsruhe, Germany). The X-ray beam (Cu-K $\alpha$ 1-radiation,  $\lambda = 0.154 \text{ nm}$ ) was provided by a graphite monochromator and a pinhole collimator with an opening of 0.8 mm. Sample-to-detector distance was 15 cm applying an irradiation time of 120 seconds.

Cyclic, thermomechanical tensile tests were performed on OCL-BA copolymer networks (standard test specimens ISO 527-2/1BB), which were programmed with a tensile tester (Zwick Z1.0, Ulm, Germany) equipped with a thermos-chamber and a

temperature controller (Eurotherm Regler, Limburg, Germany). At 60 °C samples were elongated to 50% with a strain rate of 5 mm·min<sup>-1</sup>. The temperature was decreased to 0 °C after 10 min with a cooling rate of 10 K·min<sup>-1</sup> under constant strain. Afterwards, the stress was released.

After degradation experiments, tensile tests were performed by subsequent actuation cycles between 40 °C as  $T_{sep}$  and 0 °C as  $T_{low}$  and on standard test specimens (ISO 527-2/1BB) of copolymer networks in the stress free state without an additional programming of samples. Reversible elongation ( $\epsilon_{rev}$ ) was determined by the following equation, where  $l_B$  and  $l_A$  are the lengths of the copolymer network at  $T_{low}$  and  $T_{sep}$ , respectively.

$$\epsilon_{rev} = \frac{l_B - l_A}{l_B} \cdot 100 \quad (1)$$

## RESULTS AND DISCUSSION

### Hydrolytic Degradation of Actuators

Hydrolytic degradation experiments were performed on OCL-BA copolymer networks in their programmed state (50% of elongation was applied), which exhibited a good reversible elongation (up to 12.5% in dependence of  $T_{sep}$ ) as described in reference [16]. The polymeric networks consisted of 25 wt% BA and 75 wt% OCL (mixture of OCL with  $M_n = 2.5 \text{ kg}\cdot\text{mol}^{-1}$  and  $16.0 \text{ kg}\cdot\text{mol}^{-1}$ , ratio 1:1 wt%). For this composition, the offset of thermal transition (50 °C) was distinctly separated from the temperature intended for hydrolytic degradation (40 °C), whereby the loss of actuator characteristic induced by heat can be avoided. In order to enable a fast qualitative and quantitative investigation of degradation products, accelerated degradation experiments (alkaline hydrolysis) with sodium hydroxide solution (1 M) resulting in a pH value of 13 were performed at 40 °C (as  $T_{sep}$ ).

The remaining sample mass and the swelling capacity of the polymeric networks in chloroform as swelling media as function of the degradation time were determined over a time period of 105 d and are illustrated in Figure 1.

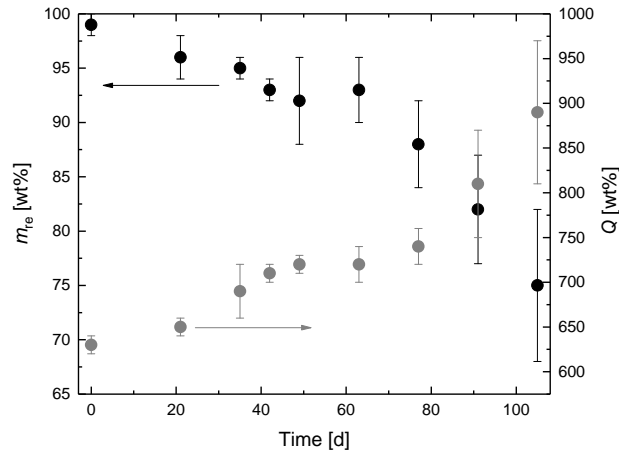


Figure 1. Determination of remaining sample mass ( $m_{re}$ , black dots) and degree of swelling ( $Q$ , grey dots) in chloroform of OCL(75)BA as function of degradation time. Error bars are related to the standard deviation of three measurements.

Here, the sample mass of OCL-BA polymer networks decreased as function of time, whereas simultaneously the swelling capacity increased. The actuators exhibited an almost linear decreasing sample mass about  $25 \pm 7$  wt% within 105 d. Furthermore,  $Q$  of OCL(75)BA increased from  $630 \pm 10$  wt% to  $890 \pm 80$  wt%. This indicates, that the polymeric network was partially degraded at pH = 13 resulting in an increasing polymer mesh size induced by a reduction of netpoint density. In contrast to this facilitated degradation utilizing alkaline hydrolysis, copolymer networks based on OCL-BA exhibited a constant material mass within one year and a mass loss of about 5 wt% after 499 d of degradation under physiological conditions (phosphate buffer solution with a pH of 7.0) [17].

In order to investigate which segments were cleaved by alkaline hydrolysis, GPC and NMR measurements were performed on the degradation solution (sodium hydroxide solution, determination of water soluble degradation products) and on the extraction solution (extraction of OCL(75)BA with chloroform, determination of water insoluble degradation products) after a degradation time of 105 d (figure 2).

$^1\text{H-NMR}$  measurements of the degradation and the extraction solution showed that compounds released in the aqueous solution were chemically different to cleaved compounds, which were not able to diffuse out of the network architecture. The components unable to diffuse out of the network architecture (extraction solution) could be identified as caprolactone segments. Characteristic signals at chemical shifts of 4.06 ppm ( $\text{CH}_2\text{-OOC}$ ), 2.30 ppm ( $\text{CH}_2\text{-COO}$ ), 1.64 ppm ( $\text{CH}_2\text{-CH}_2\text{-COO}$ ;  $\text{CH}_2\text{-CH}_2\text{-OOC}$ ), and 1.38 ppm ( $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-COO}$ ) were related to the repeating units of OCL. Furthermore, weak signals from BA units at chemical shifts of 1.67 ppm ( $\text{CH}_2\text{-CH}_2\text{-CH}_3$ ), 1.39 ppm ( $\text{CH}_2\text{-CH}_3$ ), and 0.81 ppm ( $\text{CH}_3$ ) were also detected, indicating that the degradation of OCL as crosslinker results in the release of oligo(butyl acrylate) as main chain segment. The investigation of the aqueous degradation solution showed that cleaved products generated by OCL were not able to diffuse out of the polymer networks. Here, only signals related to BA were identified.

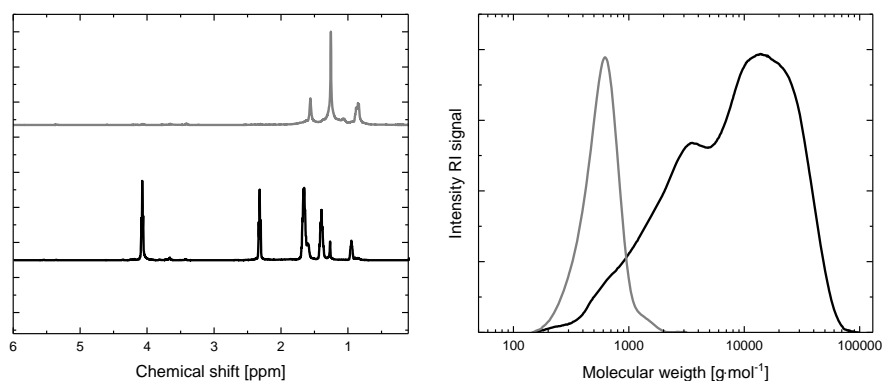


Figure 2. Analysis of degradation products in degradation media (grey) and after extraction of OCL(75)BA with chloroform (black) by means of  $^1\text{H-NMR}$  (left) and GPC (right).

The GPC measurement of the sodium hydroxide solution exhibited a distribution of molar masses of cleaved products between  $300$  and  $1000$   $\text{g mol}^{-1}$  and a  $M_n = 500 \pm 50$   $\text{g mol}^{-1}$ . Considering results based on NMR spectroscopy, water soluble fragments in the degradation solution were attributed to short oligo(butyl acrylate) segments. When the chloroform solution (extracted components from the polymeric networks) was

investigated, a bimodal broad distribution of molecular masses ranging from 400 to 50,000  $\text{g}\cdot\text{mol}^{-1}$  was detected. These components were related to smaller and bigger constituent parts of the copolymer network including OCL units.

As OCL as well as BA fractions were detected as degradation products, the OCL(75)BA composition influencing the performance of actuation has to be investigated as function of degradation time. As illustrated in figure 3, the calculated BA content exhibited no linear trend, whereby NMR measurements of the cleaved products were confirmed. The slight increase in the BA wt % integrated in the copolymer network from 0 d to 35 d indicated the hydrolytic degradation of OCL fragments. Subsequently, a pronounced reduction of BA between a degradation time of 35 d and 49 d was detected, which was related to the release of BA forming the main chain segment when the covalent netpoints were cleaved. Afterwards, the BA content exhibited again an increase as result of OCL degradation.

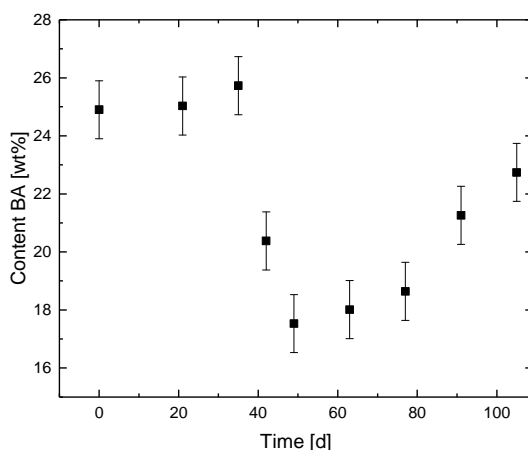


Figure 3. Determination of BA content in copolymer networks as function of degradation time. Error bars indicate the estimated error associated to the NMR method.

### Thermal Properties and Orientation of Crystalline Domains

In order to investigate how the actuation will be influenced by hydrolytic degradation, DSC measurements were performed on OCL(75)BA in dependence of the degradation period, in which especially possible changes of the broad melting transition (determining the actuation and skeleton domain) were analyzed.

Figure 4A and table 1 demonstrate the influence of alkaline hydrolysis on thermal properties of OCL(75)BA. Here, the detected  $T_{m,s}$  in the first heating run ( $T_{m,1}$  and  $T_{m,2}$ ) were affected by the thermal history of the degradation experiment (at 40 °C), whereby the division between the  $T_{m,s}$  illustrates the thermal transition of the actuator domain ( $T_{m,1}$ ) and the skeleton domain ( $T_{m,2}$ ). While  $T_{m,1}$  exhibited a slight decrease from  $39 \pm 1$  °C to  $36 \pm 1$  °C within 105 d,  $T_{m,2}$  increased from  $53 \pm 1$  °C to  $56 \pm 1$  °C. These shifts in thermal transitions indicated a cleavage of OCL segments resulting in a reduction of crystal sizes for the actuator domain (cleaved OCL chains are not able to generate big crystalline domains anymore,  $T_{m,1}$  is decreased). Simultaneously, the content of crystalline structures with lower crystal sizes in the skeleton domain is also reduced resulting in an increased  $T_{m,2}$ . Hence, it was assumed, that cleavage of ester groups in OCL segments will preferentially occur in domains of lower sizes. It has to be mentioned, that a chain scission

of semi-crystalline fractions would increase the polymer chain mobility and might enable in this way the creation of additional crystalline structures within the copolymer network.

**Table 1.** Characterization of thermal properties of OCL(75)BA during alkaline hydrolysis with determination of melting temperature ( $T_{m,s}$ ) and heat of fusions ( $\Delta H_{m,s}$ ). Given errors indicate the error of DSC measurements.

Degradation time	$T_{m,1}$ (1 <sup>st</sup> run)	$T_{m,2}$ (1 <sup>st</sup> run)	$T_m$ (2 <sup>nd</sup> run)	$\Delta H_m$ (2 <sup>nd</sup> run)
[d]	[°C]	[°C]	[°C]	[J·g <sup>-1</sup> ]
0	39 ± 1	53 ± 1	38 ± 1	31 ± 2
21	39 ± 1	53 ± 1	40 ± 1	28 ± 2
35	38 ± 1	53 ± 1	41 ± 1	31 ± 2
42	40 ± 1	53 ± 1	42 ± 1	32 ± 2
49	40 ± 1	53 ± 1	43 ± 1	31 ± 2
63	39 ± 1	56 ± 1	45 ± 1	32 ± 2
77	39 ± 1	55 ± 1	45 ± 1	30 ± 2
91	36 ± 1	56 ± 1	47 ± 1	34 ± 2
105	36 ± 1	56 ± 1	47 ± 1	32 ± 2

The thermal properties, which were detected by the second heating run of DSC measurements were not affected by the thermal history of the degradation experiment. In this case, the detected  $T_m$ s exhibited an increase from  $38 \pm 1$  °C for undegraded OCL(75)BA to  $47 \pm 1$  °C after 105 d of alkaline hydrolysis. This increase clearly demonstrates the change of crystal size ratio towards crystalline OCL domains with higher crystal dimensions. Furthermore, also the cleavage of poly(butyl acrylate) from the polymeric network would increase  $T_m$  as the BA acted here as softening agent, which reduces the thermal transition of OCL [16]. This shift of  $T_m$  exhibited no detectable influence on the heat of fusion ( $\Delta H_m$ ), which was determined in the range between 28 and 34 J·g<sup>-1</sup> demonstrating that the content of crystalline fractions kept constant. On the one hand, the cleavage of OCL ester groups could reduce the ability of reformation of crystalline domains (when the temperature is reduced) in comparison to non-degraded samples. On the other hand, new crystalline domains might be created, which could be enabled by the degradation induced increase in polymer chain mobility. Furthermore, cleaved fractions of the OCL(75)BA including crystalline domains are not able to diffuse out of the three dimensional networks in an aqueous environment and therefore would contribute to the crystallinity of the investigated copolymer networks.



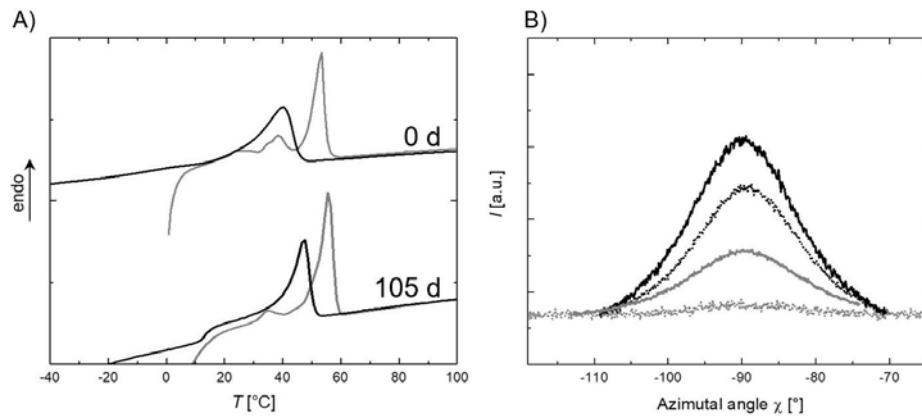


Figure 4. A) First (grey) and second (black) heating run of DSC measurements when alkaline hydrolysis of OCL(75)BA was performed for 0 d and 105 d. B) Determination of polymer chain orientation by means of WAXS measurements of OCL(75)BA after alkaline hydrolysis for 0 d (black), 21 d (black dots), 49 d (grey), and 105 d (grey dots).

An important requirement for actuators is based on the polymer chain orientation within the skeleton domain retaining the geometric information of the programmed state and which provide a directed crystallization of the actuator domain. As the degradation of OCL segments also influences the crystalline structure within the actuator domain, WAXS measurements were utilized to analyze how the cleavage of ester groups affected the orientation of crystalline domains. In figure 4B, azimuthal profiles of crystalline reflections generated by OCL are presented. The OCL(75)BA actuator exhibited decreasing intensity of the azimuthal angle as function of degradation time. As the integral peak area of the azimuthal profile correlates to the amount and intensity of oriented crystalline domains, a decreasing orientation approximately by 20% within 21 d and about 70% within 49 d of degradation was determined. After 105 d, a random alignment of crystalline OCL domains was obtained. Hence, it was assumed, that the geometric information, which was stored within the material during programming procedure disappeared and simultaneously the incapability of reversible movement as characteristic of the actuator system was expected.

### Actuation as Function of Alkaline Hydrolysis

As the alkaline hydrolysis resulted in partial degradation of OCL(75)BA with cleavage of OCL domains and loss of polymer chain orientation, it was analyzed how the performance of actuation is affected. According to the temperature intended for degradation experiments, the fixation of the programmed shape was reduced from  $98 \pm 1\%$  to  $41 \pm 4\%$ . Here, temporary netpoints within the actuation domain were cleaved resulting in a partial recovery to the permanent shape, caused by entropy elasticity. When the alkaline hydrolysis affected the polymer network (cleavage of OCL domains), the fixation decreased linearly from  $41 \pm 4\%$  at a degradation time of 0 d to  $8 \pm 5\%$  at a degradation time of 105 d. This decrease indicates that additional temporary netpoints corresponding to the skeleton domain were released as result of hydrolytic cleavage and hence, the content of geometry information which was stored within the material was reduced.

The performance of actuation was investigated between  $40\text{ °C}$  as  $T_{\text{sep}}$  and  $0\text{ °C}$  as  $T_{\text{low}}$  under stress free conditions. Figure 5A presents the heating and cooling cycles of actuators of the three different degradation time intervals: 0 h, 49 d, and 105 d. Here, the

monitored directed movement of the initial OCL(75)BA exhibited an up and down fluctuation, which was related to crystallization induced elongation (at  $T_{low}$ , to  $9.1 \pm 0.2\%$  in relation to the sample dimension at the beginning of measurement) and heating induced contraction (at  $T_{sep}$ , to  $-2.6 \pm 0.2\%$ ). When samples were degraded for 49 d, the detected directed movement was drastically reduced ranging between  $3.9 \pm 0.3\%$  (at  $T_{low}$ ) and  $-0.1 \pm 0.7\%$  (at  $T_{sep}$ ). In agreement to the determination of polymer chain orientation (loss of orientation within the polymeric network), a marginal movement of OCL(75)BA was observed at a degradation time of 105 d, which cannot be related to actuation performance. In this case, a heating induced elongation (thermal expansion) and a cooling induced contraction (thermal shrinking) was obtained. Hence, the obtained results for cyclic, thermomechanical tensile tests exhibited the loss of reversible movement as result of partially degradation of the actuator and skeleton domain.

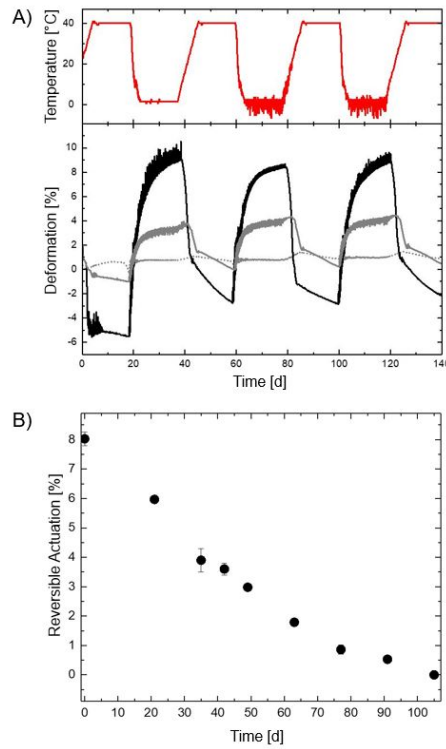


Figure 5. A) Cyclic, thermomechanical tensile tests of OCL(75)BA between 40 °C and 0 °C as function of degradation time: 0 h (black line), 49 d (grey line), 105 d (grey dots). B) Influence of alkaline hydrolysis on performance of actuation with the determination of  $\epsilon_{rev}$ . Error bars are related to the standard deviation of three measurements.

The obtained directed movement is related to a reversible elongation ( $\epsilon_{rev}$ ) of  $8.0 \pm 0.2\%$  for OCL(75)BA in the initial state as presented in figure 5B. When alkaline hydrolysis was performed on OCL(75)BA, the directed movement was drastically and almost linearly reduced as function of time. Within 35 d, the performance of actuation was halved to  $\epsilon_{rev} = 3.9 \pm 0.4\%$  and samples at a degradation time of 91 d exhibited only a marginal effect with  $\epsilon_{rev} = 0.5 \pm 0.1\%$ . A movement of  $\epsilon_{rev} = 0\%$  was reached for OCL(75)BA when alkaline hydrolysis was applied for 105 d. At this point, the requirement for directed crystallization processes, i.e. the orientation of polymer chains in the skeleton

domain, was irrecoverable (without the application of a new programming procedure) resulting in the loss of functionality.

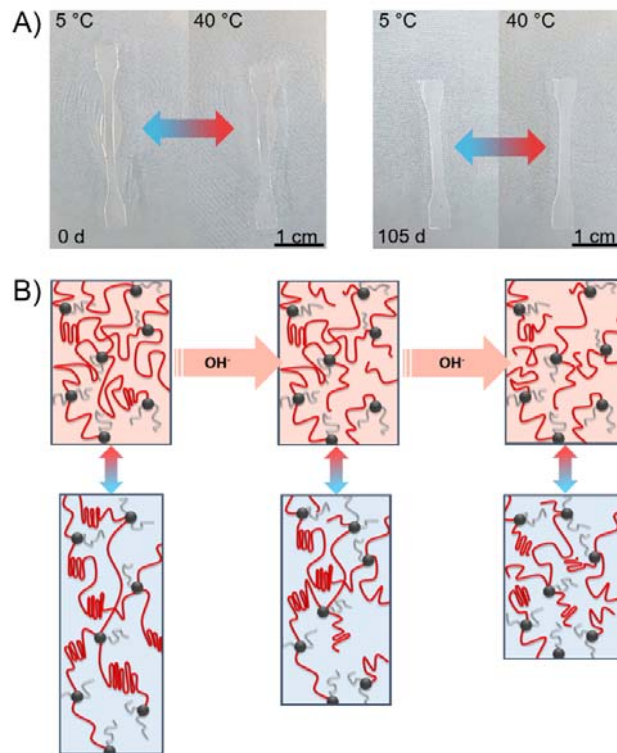


Figure 6. A) Photographs of OCL(75)BA at a degradation time of 0 d and 105 d at 40 °C and 5 °C. B) Schematic illustration of changes within the polymer network structure as result of temperature and alkaline hydrolysis. OCL (red), BA (grey), chemical netpoints (grey dots).

In Figure 6A, photographs of the OCL(75)BA actuator at 5 °C and 40 °C are presented at a degradation time of 0 d and 105 d. The demonstrator exhibited a reversible shape change before alkaline hydrolysis as result of melting-induced contraction and crystallization-induced elongation (see also Figure 6B). When the actuator was treated with sodium hydroxide solution at 40 °C, OCL chains were cleaved resulting in a decreasing content of oriented polymer chains. As result, the performance of reversible actuation was reduced. At a degradation time of 105 d, the material system exhibited no detectable macroscopic changes within a temperature interval of 40 °C and 5 °C. Here, non-oriented crystalline domains could be generated at 5 °C, which did not contribute to a directed movement resulting in the loss of functionality. In addition, the actuator exhibited a turbidity after alkaline hydrolysis, which was related to a changed light scattering behavior when crystalline domains were rearranged in the polymeric network. The degradation rate and the related lifetime of a reversible movement can be adapted by changes in the environmental conditions (e.g. degradation at another temperature, another pH value, or by an accelerated degradation by means of enzymatic cleavage of ester bonds)

## CONCLUSION

Soft actuators based on OCL and BA as copolymer networks forming components were degraded via alkaline hydrolysis at 40 °C. The copolymer network exhibited a reduced sample mass, whereby OCL fragments could be detected as degradation products. The thermal transitions of the actuator and skeleton domain were affected by the degradation procedure. While  $T_m$  of the actuator domain decreased as function of degradation time,  $T_m$  of the skeleton domain increased. By means of WAXS measurements, a rearrangement of polymer chains in the networks architecture was detected. Here, crystalline domains of OCL lost their orientation resulting in a random alignment of all polymer chains within the network architecture. Hence, OCL-BA copolymer networks exhibited a decreasing reversible elongation as function of time and subsequently the destruction of the actuation capability.

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