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High-Strain Shape-Memory Properties of Poly(Carbonate-Urea-Urethane)s Based on Aliphatic Oligocarbonates and L-Lysine Diisocyanate

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ABSTRACT

The simultaneous capability of high-strain deformation and high shape recovery ratio constitutes a great challenge in design of the shape-memory polymers. Here we report on poly(carbonate-urea-urethane)s (PCUUs) synthesized by a precursor route, based on oligo(alkylene carbonate) diols, L-lysine diisocyanate (LDI), and water vapor. When programmed with a strain of $\varepsilon_{\text{prog}} = 800\%$, the PCUU networks exhibited a one-way shape-memory effect (1W-SME) with excellent shape fixity ($> 97\%$) and shape recovery ($> 99\%$) ratios. The switching temperatures (T_{sw}) varied between 50 and 56 °C and correlated to the melting transitions of the switching domains. The obtained PCUUs capable of high-strain are interesting candidate materials for degradable biomaterials as required in smart medical devices.

INTRODUCTION

Shape-memory polymers (SMPs) can contain two types of crosslinks, which determine the permanent shape and can be based on covalent bonds or physical interactions. Thermoplastic SMPs, based on noncovalent interactions like hydrogen bonds, chain entanglement or ionic interactions, provide a high deformability but exhibit low shape recovery [1-3]. The recovery behavior strongly relates to the morphological changes of the polymer occurring during the deformation process named programming, such as orientation, structural relaxation, and chain sliding [4-6]. Therefore, to achieve high shape recovery of thermoplastic polymers, typically programming strains ($\varepsilon_{\text{prog}}$) much below the maximum of elongation at break (ε_{b}) are applied. On the other hand, covalently crosslinked SMPs exhibit much higher shape-recovery ratios (R_r), but they are capable of lower deformations, limited by the ε_{b} [2,7-9]. Thus far, only a few examples of covalently crosslinked SMPs with high recoverable strains have been reported. Copolymers based on methyl acrylate and isobornyl acrylate crosslinked by bisphenol A ethoxylate di(meth)acrylate have shown fully recoverable strains of 800% [10]. Shape-memory methyl acrylate and methyl methacrylate copolymer networks containing movable netpoints of an interlocked slide-ring structure were reported to be capable of initial deformation of 800% whereby they showed $R_f = 94\%$ and $R_r = 92\%$ [11]. In one of our previous studies we have presented poly(carbonate-urea-urethane)s (PCUUs) based on aliphatic oligocarbonate diols and isophorone diisocyanate (IPDI) with high-strain capability. It was shown, that these networks, due to the presence of both covalent and noncovalent netpoints, were able to show excellent deformability for the temporary shape up to 1000% and simultaneously high R_r [12]. Although the IPDI is known for generating less toxic degradation products in comparison to aromatic diisocyanates, its degradation products are still considered to cause some inflammatory

responses. The LDI, as a derivative of the natural amino acid L-lysine, was reported to lead to non-toxic degradation products [13]. Therefore, to improve the biocompatibility as well the biodegradability of PCUUs, in the present study the lysine diisocyanate (LDI) was implemented as a precursor of hard segment domains. Furthermore, previously reported studies have shown significant influence of the applied diisocyanate on the thermal, mechanical, and biodegradation properties [14,15]. Therefore, the influence of the LDI on the PCUUs properties in comparison to IPDI was investigated. A two-step procedure was applied. In a first step diisocyanate telechelics were obtained by reacting oligocarbonate diols with an excess of diisocyanate. Then, a moisture-curing process was applied, whereby isocyanate groups were hydrolyzed to amine groups. As a result of the reaction between newly formed amine groups and isocyanates, chain extension with the formation of urea groups took place. Side reactions occurring in this moisture-curing process between isocyanate, urea, and urethane groups result in the limited formation of biuret and allophanate netpoints [12,16]. However, these intermolecular covalent bonds are formed in limited amount, thus high deformation capability of networks is not hampered. Here we explored the influence of hard segments precursors on the morphology, thermal, and mechanical properties of PCUUs. To analyze the impact of the switching segment precursor on the properties of PCUUs, the aliphatic, highly-crystallizable oligocarbonate diols of various molecular weights and various length of the hydrocarbon chain between the carbonate linkages were selected. Furthermore, systematic studies of LDI-based PCUUs were performed to analyze the high-strain shape-memory properties such as switching temperature (T_{sw}), shape fixity (R_f), and shape recovery (R_r) ratios.

EXPERIMENT

Aliphatic oligocarbonate diols (oligo(nonamethylene carbonate), oligo(decamethylene carbonate) and oligo(dodecamethylene carbonate)) (oCDs) were synthesized following a two-step polycondensation procedure based on bis(methylcarbonate)s and α,ω -diols, described in reference [16]. Afterwards, the residual amount of the catalyst was removed from oCDs by dissolving them in chloroform and washing with a 3% aq. solution of HCl, followed by washing with distilled water and drying for 24 h at 100 °C under reduced pressure. The number average molecular weights were determined by ^1H NMR spectra and were in the range of 2100 to 3800 $\text{g}\cdot\text{mol}^{-1}$. Poly(carbonate-urea-urethane)s were created in a two-step prepolymer method. In a first step diisocyanate telechelics were synthesized by the reaction of the aliphatic oligocarbonate diols with a 3-molar excess of lysine ethyl ester diisocyanate or isophorone diisocyanate. The subsequent chain extension process was performed in a climate chamber under controlled conditions of humidity and temperature [16]. Poly(carbonate-urea-urethane)s were named **PCUU(X_nY)-Z**, where X represents the number of methylene groups in hydrocarbon chain of α,ω -diol (nona-, deca-, and dodecanediol), Y indicates the M_n of oCD in 1000 $\text{g}\cdot\text{mol}^{-1}$, and Z specify the isocyanate used (I for IPDI and L for LDI). The densities of samples were measured with an Ultra Pycnometer (Quantachrome, Odelzhausen, Germany) at 25 °C using a measurement cell with a calibration volume of 1.2657 cm^3 . The crosslinking density (ν) and average molecular weight of polymer segments between two cross-links (M_c) were determined according to the equation: $\nu = \rho / M_c$, where ρ is sample density [17]. M_c was calculated from the experimentally determined E' (storage modulus) according to the equations: $\nu = 2E'/3RT$, $E' = \rho RT/3M_c$, $\nu = E'/3RT$, where R is the gas constant and T is the temperature (K).

Cyclic, thermomechanical tests and tensile tests were conducted with standard samples (ISO 527-2/1BB) cut from films on a tensile tester Z75 (Zwick, Ulm, Germany) equipped with a thermo-chamber and a temperature controller Eurotherm control 2408 (Eurotherm Regler, Limburg, Germany). The uniaxial tensile tests were conducted at room temperature (r.t.) and 70 °C with a stretching speed of 20 mm·min⁻¹.

For the demonstration of high-strain shape-memory behavior samples were deformed at T_{prog} , which was above the melting point of the switching segments, to $\varepsilon_{\text{prog}} = 800\%$. The strain was held constant for 10 min at T_{prog} to allow relaxation, and then the sample was cooled to T_{low} with a cooling rate of 5 K·min⁻¹ and kept at $\varepsilon_{\text{prog}}$ for another 10 min. The temporary shape ε_{u} was fixed after unloading the stress. Then sample was heated to T_{high} with a heating rate of 5 K·min⁻¹ and kept at this temperature for 10 min resulting in shape recovery to ε_{p} . Afterwards the next cycle was performed. The shape fixity ratio R_f was calculated according to the equation: $R_f = \varepsilon_{\text{u}}(N)/\varepsilon_{\text{prog}}$. The capability of the material to recover the original shape was quantified by the shape recovery ratio $R_r = [\varepsilon_{\text{u}}(N) - \varepsilon_{\text{p}}(N)]/[\varepsilon_{\text{u}}(N) - \varepsilon_{\text{p}}(N-1)]$ [18]. T_{sw} was determined at the inflection point of the elongation/temperature curve at the maximum of the absolute value of $\Delta\varepsilon/\Delta T$. $T_{\text{prog}} = T_{\text{high}} = 60$ °C was applied for all samples. T_{low} was as follows: for **PCUU(12_2.1)-L** and **PCUU(10_3.8)-L** it was 0 °C, for **PCUU(10_2.8)-L** and **PCUU(10_3.8)-I** it was -10 °C, and for **PCUU(9_2.8)-L** it was -25 °C, according to the T_{cs} determined in differential scanning calorimetry (DSC) analysis. The influence of T_{low} on the shape-memory properties was investigate by applying $T_{\text{low}} = -25$ °C for **PCUU(10_2.8)-L**. The DSC, dynamic mechanical thermal analysis (DMTA), and wide angle X-ray scattering (WAXS) measurements were performed as stated in reference [12].

RESULTS AND DISCUSSION

Based on DSC analysis the glass transition temperature (T_{gs}), melting point ($T_{\text{ms}}, \Delta H_{\text{ms}}$), and crystallization temperature ($T_{\text{cs}}, \Delta H_{\text{cs}}$) of the switching phase were determined (**Table 1**). Presented data show that with an increase of the length of the polymer chain segments between the carbonate linkages in the switching domains T_{ms} as well as T_{cs} significantly increased. Based on the WAXS analysis it was shown that the degree of crystallinity (χ_{c}) of PCUU increased with increasing M_{n} of OCD as well as increasing length of the polymer chain segments between the carbonate linkages in the switching domains. A similar relation between the χ_{c} and the molecular weight of the switching segment was observed in poly(carbonate-urethane)s [19,20].

Difference in the chemical structure of IPDI and LDI has significant influence on the morphology and thermal properties of the PCUUs. Schematic presentation of the structure of both types of PCUUs is shown in the **Figure 1**. The **PCUU(10_3.8)-I** exhibited lower χ_{c} and smaller crystal size (l_{c}) compared to **PCUU(10_3.8)-L**. Furthermore, significantly lower values of T_{cs} (ΔH_{cs}) and T_{ms} (ΔH_{ms}) in comparison to **PCUU(10_3.8)-L** were observed. This can be explained by the asymmetric, cyclic structure of IPDI, which disturb the regular structure of the resulting PCUUs.

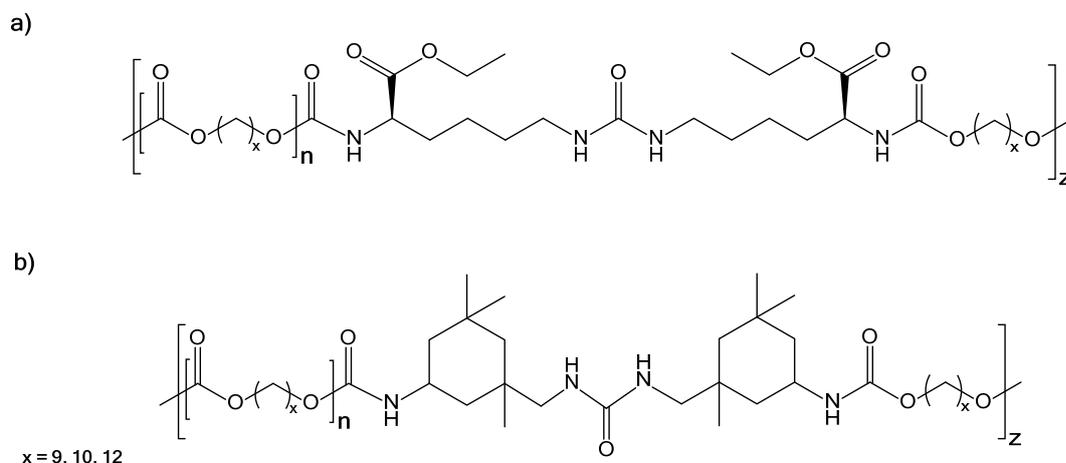


Figure 1. Proposed structure of obtained PCUUs based on **a)** LDI and **b)** IPDI (a mixture of isomers of IPDI was used and only a simplified structure is presented).

Table 1. Thermal and morphological analysis of LDI-based PCUUs.

Sample	T_g (°C)	T_{mS} (°C)	ΔH_{mS} (J/g)	T_{cS} (°C)	ΔH_{cS} (J/g)	l_c ^{a)} (nm)	χ_c ^{b)} (%)
PCUU(12_2.1)-L	nd ^{c)}	54 ± 1	42 ± 1	14 ± 1	44 ± 1	13.0 ± 0.2	25.2 ± 0.2
PCUU-(10_3.8)-L	-40 ± 1	47 ± 1	41 ± 1	16 ± 1	45 ± 1	13.4 ± 0.2	24.9 ± 0.2
PCUU-(10_3.8)-I	-45 ± 1	43 ± 1	32 ± 1	7 ± 1	36 ± 1	11.8 ± 0.2	19.4 ± 1.2
PCUU-(10_2.8)-L	-37 ± 1	48 ± 1	32 ± 1	-1 ± 1	38 ± 1	13.2 ± 0.2	23.0 ± 0.2
PCUU-(9_2.8)-L	-42 ± 1	44 ± 1	34 ± 1	-15 ± 1	33 ± 1	15.0 ± 0.2	22.5 ± 0.0

^{a)} l_c – crystal size, determined by WAXS analysis. ^{b)} χ_c – degree of crystallinity, determined by WAXS analysis. ^{c)} T_g was not observed during applied DSC measurement conditions.

The influence of the crosslinking density (ν) on the properties of PCUUs was investigated by means of DMTA (**Table 2**). The **PCUU(10_3.8)-I** has shown the highest ν among investigated samples, significantly higher than the LDI-analogue. Lower ν of **PCUU-(10_3.8)-L** could be a result of the steric hindrance caused by ethyl ester side groups close to the hard segments of the polymer chains. Among the LDI-based PCUUs, the ν decreased when the length of the hydrocarbon chain between the carbonate linkages in the soft segment chain decreased, whereas the values of average molecular weight of the polymer chain segments between two crosslinks (M_c) increased (e. g. samples **PCUU(10_2.8)-L** and **PCUU(9_2.8)-L**). It was reported that oligo(alkylene carbonate) diols containing 9 and 10 methylene groups between the carbonate linkages form a zigzag structure.[21] Therefore, the even or odd number of methylene groups in the soft segment of PCUUs has significant influence on the potential formation of hydrogen bonds within hard and soft segment domains. In case of PCUUs containing an even number of methylene groups in soft segment repeating units (e.g. **PCUU(10_2.8)-L**) the carbonyls in the carbonate groups are located in both sides of the main polymer chain. As a result polymer chains have better geometric fit, which results in a more regular structure. In case of **PCUU(9_2.8)-L** polymer chains are not able to form as regular structure, which significantly disturb the formation of hydrogen bonds within the hard segments and results in a lower crosslinking density. This could also be confirmed by much lower values of T_c and T_g in case of PCUU-9

when compared to PCUU-10. A similar behaviour was observed in case of polyester-based polyurethanes obtained from adipic and pimelic acids as soft segments.[22] In case of **PCUU(12_2.1)-L** lower values of ν compared to other investigated samples were observed. This might be the result of the relatively low molecular weight of the switching segment, which could lead to lower phase separation between hard and soft segments and, as a consequence, to lower crosslinking density between hard domains.

Table 2. Crosslinking density (ν) and average molecular weight of polymer segments between two crosslinks (M_c) estimated based on storage moduli.

Sample	ρ (g·cm ⁻³)	M_c ^{a)} (g·mol ⁻¹)	ν ^{b)} (10 ⁻⁴ ·mol·cm ⁻³)
PCUU(12_2.1)-L	0.845 ± 0.004	3300 ± 100	2.6 ± 0.2
PCUU(10_3.8)-L	0.818 ± 0.002	2100 ± 100	4.0 ± 0.3
PCUU(10_3.8)-I	0.998 ± 0.005	1600 ± 100	6.0 ± 0.4
PCUU(10_2.8)-L	0.874 ± 0.006	2100 ± 100	4.0 ± 0.3
PCUU(9_2.8)-L	0.850 ± 0.005	2900 ± 100	3.0 ± 0.2

^{a)} M_c - number average molecular weight of polymer segments between two crosslinks determined by DMTA. ^{b)} ν - crosslinking density determined by DMTA.

The deformation capability of the samples was examined in uniaxial tensile tests at r.t. and at $T > T_m$ (70 °C) (**Table 3**). All LDI-based samples have similar mechanical properties at r.t., with tensile strength (σ_m) in the range between 22 and 28 MPa, and elongations at break (ε_m) of around 1000%. Above T_m of the crystallisable switching segments (70 °C) the Young's moduli (E) dropped significantly from 25-50 MPa to 1-2 MPa. In addition, σ_m decreased to 2-5 MPa, indicating a strong influence of crystalline switching domains on the mechanical strength of the polymer. Furthermore, no significant change of ε_m at 70 °C was observed when compared to the values at r.t., which indicates a strong interaction within the hard segment domains. In case of **PCUU(10_3.8)-I**, slightly lower ε_m and significantly higher values of σ_m and E were observed in comparison to **PCUU(10_3.8)-L**. This can be explained by the rigidity of cycloaliphatic IPDI. It was also reported that IPDI-based poly(urea-urethane)s are prone to form longer urea blocks within hard segments, which significantly increases the mechanical properties of the polymer [23].

Table 3. Mechanical properties of PCUUs obtained from different oCDs at r.t. and at 70 °C.

Sample	r.t.			70 °C		
	E (MPa)	σ_m (MPa)	ε_m (%)	E (MPa)	σ_m (MPa)	ε_m (%)
PCUU(12_2.1)-L	48 ± 4	22 ± 1	1020 ± 20	1.3 ± 0.1	1.8 ± 0.1	900 ± 5
PCUU(10_3.8)-L	36 ± 12	27 ± 4	1050 ± 40	2.1 ± 0.2	4.9 ± 1.8	1200 ± 140
PCUU(10_3.8)-I	34 ± 2	38 ± 6	900 ± 100	3.5 ± 0.3	10.4 ± 2.2	960 ± 80
PCUU(10_2.8)-L	25 ± 5	26 ± 1	1080 ± 25	1.8 ± 0.1	2.3 ± 0.3	870 ± 60
PCUU(9_2.8)-L	50 ± 6	28 ± 2	1060 ± 10	0.8 ± 0.1	1.6 ± 0.3	1180 ± 70

The shape-memory performance was determined in cyclic, thermomechanical experiments. The macroscopic changes of the strain of a sample during shape-memory effect (SME) measurement is shown in **Figure 2a** exemplarily for **PCUU(10_3.8)-L** with $\varepsilon_{\text{prog}} = 800\%$. **Figure 2b** shows the

average results of cyclic, thermomechanical measurements of all investigated PCUU networks. The first cycle of measurements was not taken under consideration for the analysis of the shape-memory properties, because of the thermal history, as well as due to the effect of the amorphous chains flow, plastic deformation and relaxation [20]. Therefore, values of shape fixity ratios (R_f) and shape recovery ratios (R_r) were calculated based on the results from the second to fourth cycles of measurements. Among LDI-based PCUU networks, an increase of the length of the hydrocarbon chain in α,ω -diol caused an increase of values of R_f . For example for **PCUU(9_2.8)-L** and **PCUU(10_2.8)-L** they were $97.8 \pm 1\%$ and $98.9 \pm 0.1\%$, respectively. This can be attributed to an odd structure of chains of switching segments of **PCUU(9_2.8)-L**, which have lower ability for crystallization. Values of R_r in case of **PCUU(10_2.8)-L** were slightly lower compared to **PCUU(9_2.8)-L**. This can be explained by the influence of covalent bonds formed within the hard segment domains. It was previously reported that samples of poly(carbonate-urea-urethane)s containing nine methylene groups between the carbonate linkages are much more prone to creation of allophanate and biuret crosslinks [16]. This suggests that good shape-memory properties of samples based on even number (10 or 12) of methylene groups in the repeating unit of the switching segments are related to the netpoints based on physical interactions between the hard segments.

The switching temperature (T_{sw}) varied between 50 and 56 °C and increased significantly with increasing hydrocarbon chain length in the repeating unit of the switching segment. Remarkably, all the samples based on LDI exhibited $R_f > 97\%$ and $R_r > 99\%$ after five cycles (**Figure 2a**). Due to the lower ability to crystallization of **PCUU(10_3.8)-I** compared to **PCUU(10_3.8)-L**, lower capability of fixation of the temporary shape (R_f of 97%) was observed. On the other hand, R_r was higher in comparison to the one exhibited by **PCUU(10_3.8)-L** due to the high value of ν . The T_{sw} of **PCUU(10_3.8)-I** decreased in comparison to **PCUU(10_3.8)-L** from 53 to 47 °C, which corresponds to differences in T_m of switching segment domains.

Moreover, there may be a potential influence of T_{low} on R_f and R_r . To explore the influence of T_{low} on the shape-memory properties a cyclic, thermomechanical measurement of the sample **PCUU(10_2.8)-L** was performed with $T_{low} = -25$ °C (the lowest T_{low} among investigated samples, which was applied for **PCUU(9_2.8)-L**). It was shown, that the R_r increased slightly (from 99.2 to 99.5%) with $T_{low} = -25$ °C in comparison to R_r obtained with $T_{low} = -10$ °C. However, these differences are within the margin of error. The $R_f = 98.7 \pm 0.5\%$ was the same for both investigated samples, independently from the T_{low} applied. This indicates that originally chosen T_{low} , which were around 10 to 15 °C below the T_m of each sample, were sufficient to effectively fix the temporary shape. Also the $T_{sw} = 53 \pm 1$ °C was not influenced by the change of applied T_{low} .

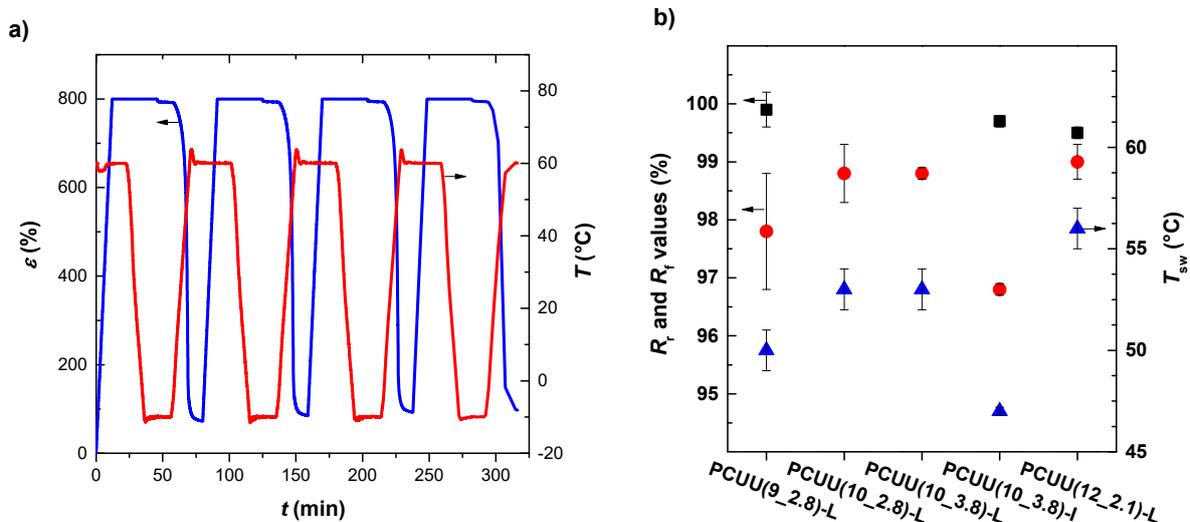


Figure 2. (a) Macroscopic changes of the strain of PCUU(10_3.8)-L during 4 cycles of thermomechanical SME measurement ($\varepsilon_{\text{prog}} = 800\%$). (b) R_r , R_f and T_{sw} for PCUUs in case of $\varepsilon_{\text{prog}} = 800\%$.

CONCLUSIONS

A shape-memory poly(carbonate-urea-urethane) capable of high deformability (800%) and a simultaneous high shape-memory recovery ratio $R_r \geq 99\%$ is presented. A high value of R_r was related to both of the types of the permanent crosslinks: physical interactions and covalent bonds between the hard segment domains. An increase of shape fixity ratio from 97 to 99% was achieved in LDI-based PCUUs in comparison to IPDI-based PCUUs. The switching temperatures (T_{sw}) of LDI-based PCUUs varied between 50 °C and 56 °C and corresponded to the T_m of the switching segments. Obtained PCUUs are interesting candidate materials for potential medical applications such as biodegradable surgical sutures or vascular stents.

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