J Mater Sci: Mater Med (2011) 22:2147–2154
DOI 10.1007/s10856-011-4404-6

Upscaling the synthesis of biodegradable multiblock copolymers capable of a shape-memory effect

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Received: 1 March 2011 / Accepted: 25 July 2011 / Published online: 11 August 2011

Abstract Thermoplastic, phase-segregated multiblock copolymers (MBC) with shape–memory capability consisting of poly(ε-caprolactone) (PCL) switching segments and poly(*p*-dioxanone) (PDO) or poly(ω-pentadecalactone) (PPD) hard segments were prepared on a scale of several kilograms following a newly developed upscaling procedure. Dihydroxytelechelic poly(ether)esters were coupled by an aliphatic diisocyanate gaining products of sufficiently high molecular weights. The obtained biodegradable MBC exhibited good elastic properties and a shape–memory effect (SME) with a switching temperature (T_{sw}) around body temperature. The yield of the synthesis could be improved and reaction time reduced, while mechanical and shape–memory properties were not affected. These multifunctional materials, which are now available in a larger scale have a high application potential as smart implant materials especially for minimally invasive surgery.

1 Introduction

Biodegradable thermoplastic polymers with a thermally-induced shape–memory effect (SME) belong to a new class of multifunctional materials [1–7]. The combination of the shape–memory capability with other functionalities such as biocompatibility, controlled drug release, and biodegradability of the material can be selectively adjusted to the demands of a specific application. Such polymeric materials are explored today for various medical applications including surgical devices, and controlled drug release systems [7–11]. Their biodegradability makes these multifunctional polymers promising candidate materials for regenerative therapies [12, 13].

Shape–memory polymers (SMP) can change their shape from a temporary shape, which was created by a previous programming procedure, into a permanent shape, when they are exposed to a suitable external stimulus such as heat or light [1, 14, 15]. The permanent shape is defined by the initial processing step and can be changed in thermoplastic SMPs. In phase-segregated multiblock copolymers (MBC) the domains related to the highest thermal transition (hard domain) ensure the mechanical integrity of the material and its permanent shape. If the corresponding transition temperature (T_{perm}) is exceeded, the material's integrity is lost and the permanent shape can be altered. The domains associated to the second highest thermal transition (switching domains) permit a reversible fixation of a temporary shape. Here, we report on the manufacturing of two different SMPs based on poly(ether)ester urethanes in a larger scale (kg scale). In both MBC the switching segment was represented by crystallizable poly(ε-caprolactone) (PCL) segments while the crystallizable hard segments were either poly(*p*-dioxanone) (PDO) or poly(ω-pentadecalactone) (PPD) segments.

In contrast to the MBC PCL-*bl*-PDO, which exhibits a faster hydrolytic degradability, the MBC PCL-*bl*-PPD is hydrolytically more stable and also more hydrophobic. MBCs with good shape–memory properties could be obtained by using linear macrodiols having a number average molecular weight (M_n) between 2000 and

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5000 g mol^{-1} and a hard segment weight content (ratio of the macrodiols) of 50 wt% in case of PCL-*bl*-PDO and 40 wt% in case of PCL-*bl*-PPD [4, 7].

In order to advance the application strategies with the objective of product design the conditions for thermoplastic processing of these promising polymeric materials have to be investigated and quantities in the range of several kilograms are required. The synthesis of PCL-*bl*-PDO was described to be carried out in 1,2-dichloroethane (DCE) with 2,2(4),4-trimethyl-hexamethylene diisocyanate (TMDI) as coupling reagent without application of a catalyst [7]. The use of tin catalyst was relinquished to avoid residual tin traces in medical grade polymers but accepting longer reaction times. TMDI was applied as coupling reagent to minimize interactions between the diurethane bridges by disturbing potential interactions (e.g. hydrogen bonds) with the methyl groups. The DCE's boiling point of 83°C was intended to keep the reaction temperature low enough to minimize the formation of side products such as allophanates and biurets during the long reaction time of several weeks. The work-up was conducted by precipitation of the polymers in a tenfold excess of hexane. Similar reaction conditions have been applied also for other copolyesters [1, 3, 7, 16]. However, the procedures used so far for the synthesis of these MBCs and the underlying macrodiols were not suitable for the preparation of larger quantities as very large amounts of solvents and non-solvents (for the purification stages) would be required and usually non-uniform polymer lumps or fibers were obtained from precipitation, which are difficult to process in large scale. Therefore, new efficient procedures with the necessary reliability, and manageability were necessary for the synthesis of MBCs on a scale of 1–3 kg. The challenge was mainly the achievement of reproducible high values of M_n to ensure good elastic properties. Furthermore, the focus was on the reduction of the amounts of solvents and non-solvents, the reduction of reaction time with regard to economic efficiency and minimization of side reactions, and the processability of the raw material after work-up.

In this paper we report on a new upscaled procedure (UP) for the syntheses of the afore mentioned two MBCs and the required macrodiol precursors, which allowed the production of the copoly(ether)esters urethanes in the scale of several kilograms while retaining good shape–memory properties. The influence of the large scale synthesis method on the chemical, thermal, and thermomechanical properties of the MBCs was investigated by means of FTIR, NMR, GPC, DSC, tensile tests, and cyclic, thermomechanical measurements. The obtained results were discussed and compared with the properties of the MBCs manufactured previously according to the established small scale procedure (SP).

2 Materials and methods

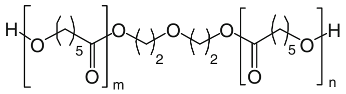
2.1 Materials

Poly(ε-caprolactone) diol, (**1**, PCL-diol, trade name CAPA2205: $M_n = 2000$ g mol^{-1}; trade name CAPA2304: $M_n = 3000$ g mol^{-1}) were obtained from Solvay, Waringthon, UK. *p*-dioxanone (*p*DX, purity >99%) was purchased from Daiwa Kasei Ind., Japan and ω-pentadecalactone (PDL, trade name SUPRA, 98% purity) was purchased from Th. Geyer, Germany. Octane diol and hexamethylene diisocyanate (HDI, purity >99%) were provided by Fluka, Taufkirchen, Germany. Dibutyltin oxide (DBTO, 98% purity) and dibutyltin dilaurate (DBTDL, purity >95%) were purchased from Aldrich, Taufkirchen, Germany. Dimethylcarbonate (DMC, purity >98%) was obtained from Acros Organics, Geel, Belgium, the ethyl alcohol (purity >94%) was purchased from Berkel AHK Berlin, Germany and the liquid nitrogen was provided by Linde AG, Germany.

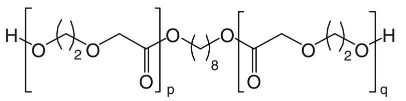
2.2 Synthesis of PDO and PPD macrodiols (UP)

A general procedure for the polymerization of *p*DX using octane diol as initiator but without the addition of a catalyst was as follows: *p*DX (1000 g) was heated to 108°C under nitrogen atmosphere. After addition of octane diol (104 g, calculated to result in a M_n of approximately 4500 g mol^{-1}), the reaction mixture was stirred for 21 days at this temperature. Then the polymer melt was divided into four partitions and each was diluted in 3 L DMC and subsequently 1 L ethyl alcohol was added. The PDO-diol **2** precipitated in a refrigerator at −12°C over night (yield 68–81 wt%).

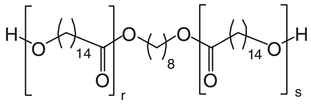
A general procedure for the polymerization of PDL was as follows: PDL (3200 g) was heated to 130°C. After addition of dried octane diol (250 g, calculated to result in a M_n of approximately 3000 g mol^{-1}) and DBTO catalyst, the reaction mixture was stirred for 21 days at this temperature. Afterwards the polymer melt was subdivided into four partitions, whereupon each partition was diluted in 2 L DMC. Finally, the PPD-diol **3** was precipitated in a five-fold excess of a mixture of ethyl alcohol/water (50/50 vol%). After drying in vacuum a yield of 84–94 wt% was reached.



poly(ε-caprolactone) diol **1**



poly(*p*-dioxanone) diol **2**



poly(*ω*-pentadecalactone) diol **3**

2.3 Synthesis of PCL-*bl*-PDO (UP) and PCL-*bl*-PPD (UP)

The synthesis of PCL-*bl*-PDO (UP) MBCs (**4** in Scheme 1) was carried out as follows: about 500 g (0.108 mol) PDO-diol, 500 g (0.250 mol, CAPA2205) PCL-diol, 73.6 g (0.438 mol) HDI, and 0.160 g (0.253 mmol) DBTDL were dissolved in 2.5 L DMC and reacted at 85°C for 3 days. The PCL-*bl*-PDO was obtained by precipitation in liquid nitrogen and drying under vacuum (yield 95 wt%).

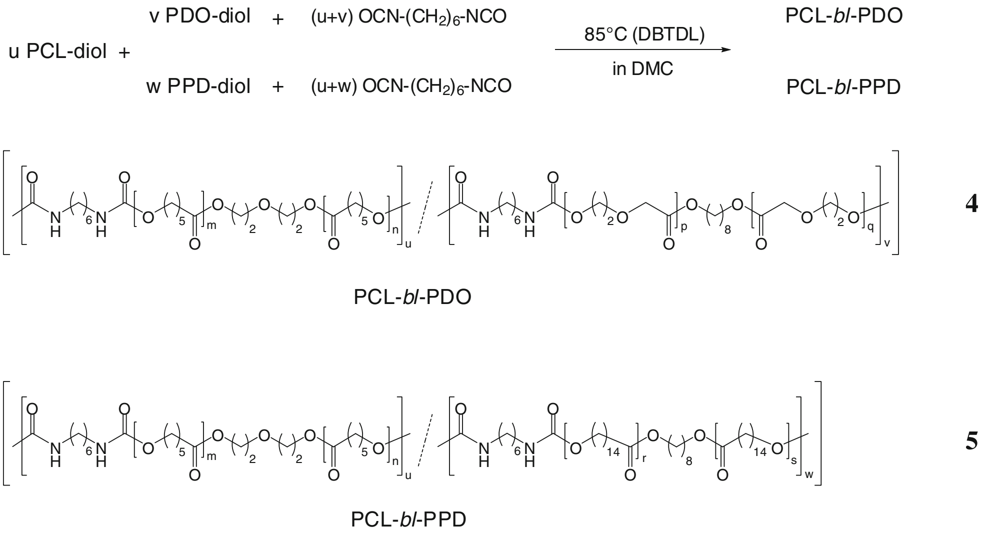
The synthesis of PCL-*bl*-PPD (UP) MBCs (**5** in Scheme 1) was carried out as follows: about 400 g (0.093 mol) PPD-diol, 600 g (0.200 mol, CAPA2304) PCL-diol, 69.96 g (0.416 mol) HDI, and 0.160 g (0.253 mol) DBTDL were dissolved in 2.5 L DMC and reacted at 85°C for 3 days. The PCL-*bl*-PPD (UP) was obtained by precipitation in liquid nitrogen and drying under vacuum (yield 95 wt%). Analogously, multiblock polymers (MBP) were synthesized, which consisted of only one type of dihydroxy telechelic precursor [PCL-MBP (UP) and PDO-MBP (UP)], serving as reference samples in analytical measurements.

2.4 Characterization methods

FTIR-spectroscopic measurements were recorded on a Nicolet Magna 550 (Thermo Electron Corp., USA) spectrometer with a single diamond ATR crystal (SensIR Technologies, USA). The spectrometer is operated with a He–Ne-laser at 632.6 nm 1 mW; aperture 100; detector: DTGS KBr, light source: IR Everglow™.

^{1}H-NMR spectroscopic experiments were recorded on an Avance 500 (Bruker Bio Spin, USA) spectrometer at RT in $CDCl_3$ (99.8 wt%, Deutero GmbH, Germany) containing tetramethylsilan as an internal standard.

Multidetector GPC measurements were performed using chloroform at 35°C as eluent with a flow rate of 1 mL min^{-1} and 0.2 wt% toluene as internal standard. The system was equipped with a precolumn, two 300 mm × 8.0 mm linear M columns (Polymer Standards Service GmbH, Mainz, Germany, PSS) an isocratic pump 2080 and an automatic injector AS 2050 (both Jasco, Tokyo, Japan). Two detectors were used: a RI detector Shodex RI-101 (Showa Denko, Japan) and the dual detector T60A (Viscotek Corp., USA), which were combined by a split. The molecular weights were



Scheme 1 Reaction scheme of synthesis of the multiblock copolymers PCL-*bl*-PDO and PCL-*bl*-PPD from poly(ε-caprolactone), poly(*p*-dioxanone), poly(*ω*-pentadecalactone) diols and HDI

determined using a universal calibration with polystyrene standards with M_n between 580 and 975000 g mol^{-1} (PSS) and with the help of the SEC software WINGPC 6.2 (PSS).

DSC experiments were performed on a Netzsch DSC 204 Phoenix (Selb, Germany). Samples for standard thermal characterization were heated from 20 to 150°C, then cooled to −100°C and reheated to 150°C. Thermal transitions were determined from the second heating (T_g, T_m) and first cooling run (T_c). All heating and cooling procedures were performed with a constant heating and cooling rate of 10K min^{-1}.

Test specimens were produced with a polymer press (type 200 E, Dr. Collin, Ebersberg, Germany) at 100°C under a pressure of 90 bar for 4 min. The film thickness was typically between 0.3 and 0.7 mm. Specimen of 1BB type according to European Standard for tensile test (DIN EN ISO1BB) were cut with a punching tool, $I_0 = 20$ mm, width 2 mm.

The mechanical properties and cyclic, thermomechanical tests of the polymers were conducted on a Z 1.0 and a Z005 (Zwick GmbH, Ulm, Germany) tensile tester equipped with a load sensor of 200 N and a thermo chamber with a temperature controller (Eurotherm Regler, Limburg, Germany). All tensile tests were performed with a preload of 0.03 N and a strain rate of 5 mm min^{-1}. Results were determined as average values with standard deviation from at least four measurements.

Stress-controlled, cyclic thermomechanical tests were performed as follows [17, 18]: the sample was stretched at T_{high} (55°C) to a maximum elongation ε_m of 150% at an elongation rate of 10 mm min^{-1}. After 5 min the stretched sample was cooled to T_{low} (0°C) under stress-control and kept for 15 min at this temperature. The fixed sample was unloaded to $\sigma = 0$ MPa and the temperature was raised to T_{high} at a heating rate of 5K min^{-1} and kept for 10 min. This program was repeated 3 times with the same sample ($N = 3$). The strain fixity rate R_f and the strain recovery rate R_r were calculated from Eqs. 1 and 2, respectively, whereas $\varepsilon_l(N)$ is the tensile strain of a loaded sample after cooling in a cyclic, thermomechanical experiment in the Nth cycle, $\varepsilon_u(N)$ is the strain in the stress-free state after the retraction of the tensile stress in the Nth cycle, $\varepsilon_p(N-1)$ and $\varepsilon_p(N)$ are the strain of the sample in two successively passed cycles in the stress-free state.

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

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

3 Results and discussion

3.1 Upscaling of the synthesis procedures

PDO-diols as well as PPD-diols were synthesized as linear precursors by means of ring-opening polymerization of the cyclic monomers using a low-molecular weight diol as initiator [19]. The ring-opening polymerization of *p*DX is described with ethylene glycol as initiator in the melt at 110°C without a catalyst [3]. Different aliphatic diols with a lower affinity to water were examined as a substitute for ethylene glycol. The solid 1,8-octane diol was chosen because it can be pulverized and is easy to proportionate and to dry in vacuum. Due to the good handling in the PDO synthesis, 1,8-octane diol was applied as initiator in the synthesis of PPD as well. A higher concentration of the polymer solution and a lower amount of the non-solvents compared with the work-up procedure according to SP was enabled by dilution of the clear, viscous polymer melts in DMC and the precipitation of the PDO and PPD diols by addition of ethyl alcohol, respectively an ethyl alcohol/water mixture. Additionally, considerable yield losses could be avoided during this purification step. By applying UP the batch size was enlarged resulting in more than 3 kg of the macrodiol products while the yield was increased by 5–20 wt% compared to SP (Table 1).

The phase-segregated MBCs were synthesized by coupling of the respective macrodiols with aliphatic diisocyanates in a polyaddition reaction resulting in copoly(ether)ester urethanes according to Scheme 1.

TMDI was substituted by the more reactive HDI to shorten reaction times. The reaction time could be reduced from about 28 to only 3 days by using DBTDL as a catalyst. A 4 L double-coated reaction vessel with thermostat heating (water) and intensive mixing by means of a spiral agitator was applied. However, in previous experiments a corrosive behavior of the DCE on steel components was observed. The replacement of the DCE by DMC led to an essential extension of the durability of all metal parts in the system. During the work-up the reaction solution (20% w/v polymer in DMC) was pumped into 50–60 L of inexpensive liquid nitrogen. The frozen reaction solution was then freeze-dried resulting in a granular product with a grain size of about 3–7 mm and saving solvents and time. The obtained granulated materials could be simply processed by extrusion or injection molding without other preconditioning. The UP led to products of sufficiently high M_n, which was comparable with the M_n obtained after SP (Table 1). Furthermore, the adjusted work-up procedure had the advantage of allowing the handling of larger amounts of MBCs by using less solvent.

3.2 Chemical analysis of PCL-*bl*-PDO (UP) and PCL-*bl*-PPD (UP)

The MBCs were characterized by GPC, IR, and NMR. M_n of the synthesized PCL-*bl*-PDO (UP) determined by GPC reached values between 18000 and 37000 g mol^{-1} with a polydispersity between 3.9 and 4.4. PCL-*bl*-PPD (UP)

Table 1 Comparison of different approaches (small scale procedure SP applied according to established literature procedure, new upscale procedure UP) for the synthesis of linear macrodiol precursors and multiblock copolymers thereof: batch size, reaction temperature (T_R), reaction time (t_R), yield, and number averaged molecular weight (M_n) of the product determined by GPC measurements

Polymer-ID[a] and synthesis approach	Batch size (g)	T_R (°C)	t_R (d)	Yield (%)	M_n (g mol^{-1})[a]
PDO-diol (SP)[b]	400–500	105	19–27	50–75	2900–6200[f]
PDO-diol (UP)[c]	ca. 3200	108	21	68–81	2800–4900[f]
PPD-diol (SP)[b, c]	200	130	19–27	50–75	4900[f]
PPD-diol (UP)[b, d]	ca. 3200	130	21	84–94	4000–4400[f]
PCL-*bl*-PDO (SP)	250	83	>28	60–80	14000–25000
PCL-*bl*-PDO (UP)[e]	1000	85	max. 3	95–99	18000–37000
PCL-*bl*-PPD (SP)	250	83	>28	60–80	20000–32000
PCL-*bl*-PPD (UP)[e]	1000	85	max. 3	95–99	28000–46000

[a] Polymer segments: poly(ε-caprolactone) (PCL), poly(*p*-dioxanone) (PDO), poly(*ω*-pentadecalactone) (PPD), a multiblock copolymer is indicated by '*bl*' between the polymer segments the involved blocks are consisting of

[b] Residual monomer 2.5–5.0 wt%

[c] Residual monomer ≤1.2 wt%

[d] Dibutyl tindioxide catalyst applied

[e] Dibutyl tindilaurat catalyst applied

[f] Apparent M_n determined by standard calibration using polystyrene standards

having M_n values between 28000 and 46000 g mol^{-1} was synthesized with a polydispersity between 1.9 and 3.1 (Table 1).

The overall composition of the synthesized MBCs corresponded to the amounts of the used starting materials due to a nearly complete conversion rate (yield >95%), which was confirmed by means of IR and NMR spectroscopy. In order to assign the IR bands of the different precursors in presence of the urethane group (amid II band at 1525 cm^{-1}) the IR spectra of PCL-MBP (UP), PDO-MBP (UP), a blend of both MBP, and PCL-*bl*-PDO (UP) were compared in Fig. 1. Three typical IR bands for the PDO component (1430 cm^{-1}, 873 cm^{-1}, and 850 cm^{-1}) and for the PCL component (1416 cm^{-1}, 1165 cm^{-1}, and 960 cm^{-1}) could be identified.

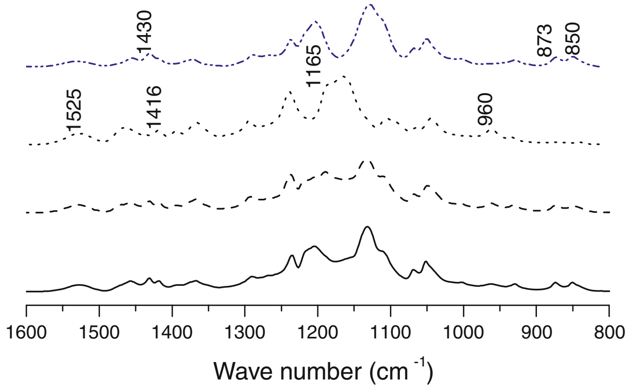


Fig. 1 IR absorption spectra of different multiblock polymer samples PDO-MBP (UP) (*dashed-dotted line*), PCL-MBP (UP) (*dotted line*), a 1:1 blend of PCL- and PDO-MBPs (UP) (*dashed line*), and PCL-*bl*-PDO (UP) MBC (*solid line*)

In Fig. 2 the ^{1}H-NMR-spectrum of a PCL-*bl*-PDO (UP) is shown with the assignments of the signals corresponding to the PCL and PDO component. The signals from the $H_{H(b)}$ and $H_{H(c)}$ CH_2 groups of the diurethane bridge in the range $\delta = 1.25$–1.65 ppm were overlapped by the dominating CH_2 signals of the PCL, the signals at $\delta = 3.65$ and 4.18 ppm originated from the CH_2 groups of the diethylene glycol, which was used as initiator for the ring-opening polymerization of ε-caprolactone.

A chromatographic fractionation of MBCs was carried out with the help of a newly developed gradient method [20]. MBCs were investigated to gain information on the extent of chemical heterogeneity of the samples under the assumption that the influence of the solvent (different solubilities of the diols) is crucial for the chemical composition. However, the MBCs were found to be composed homogeneously to an extent, which was comparable with the MBCs synthesized by SP.

3.3 Thermal properties of the MBCs

The thermal properties of the MBPs and MBCs were determined by DSC measurements. All three precursor diols are semicrystalline. Both, the PDO-MBP (UP) and the PCL-MBP (UP) exhibit a glass transition temperature (T_g) and a melting point (T_m). However, for PPD-MBP (UP) only a T_m was found in DSC thermogramms. Typical DSC curves are shown in Fig. 3.

T_m of these semicrystalline macrodiols is dependent on the block length reaching values between 89 and 98°C for the PDO-diol, between 34 and 47°C for PCL-diol and between of 81 and 93°C for the PPD-diol. For PCL-*bl*-PDO

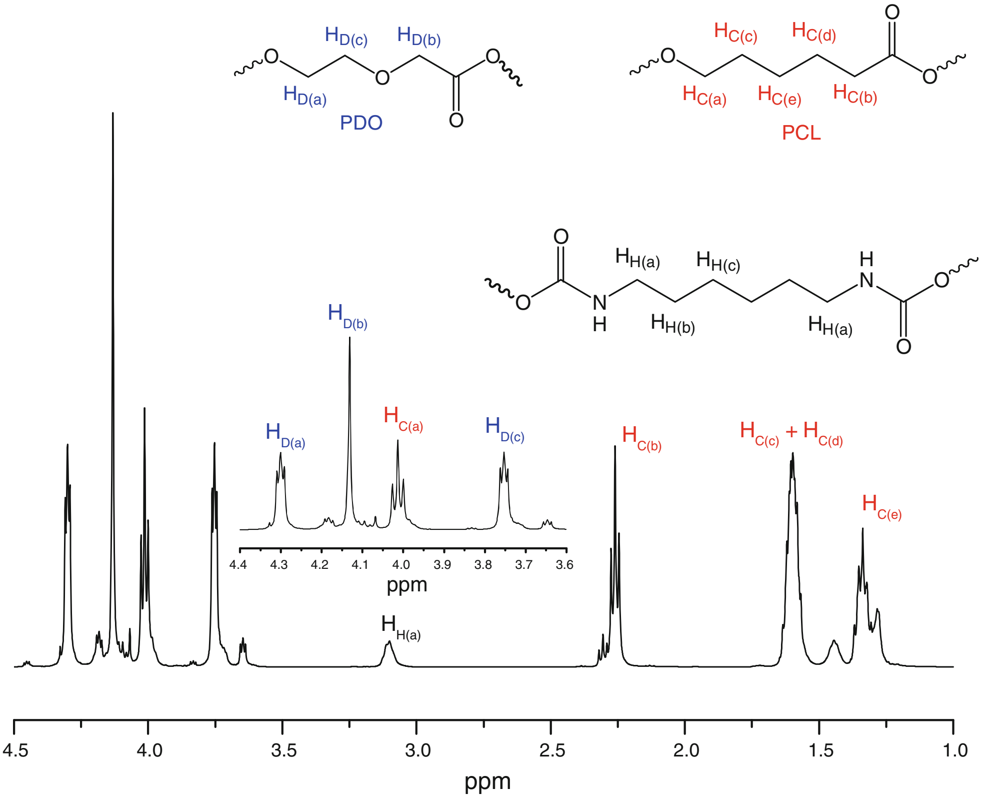


Fig. 2 ^{1}H-NMR spectrum of PCL-*bl*-PDO (UP) with the assignments of the typical protons signals of the PCL and PPO blocks as well as diurethane units

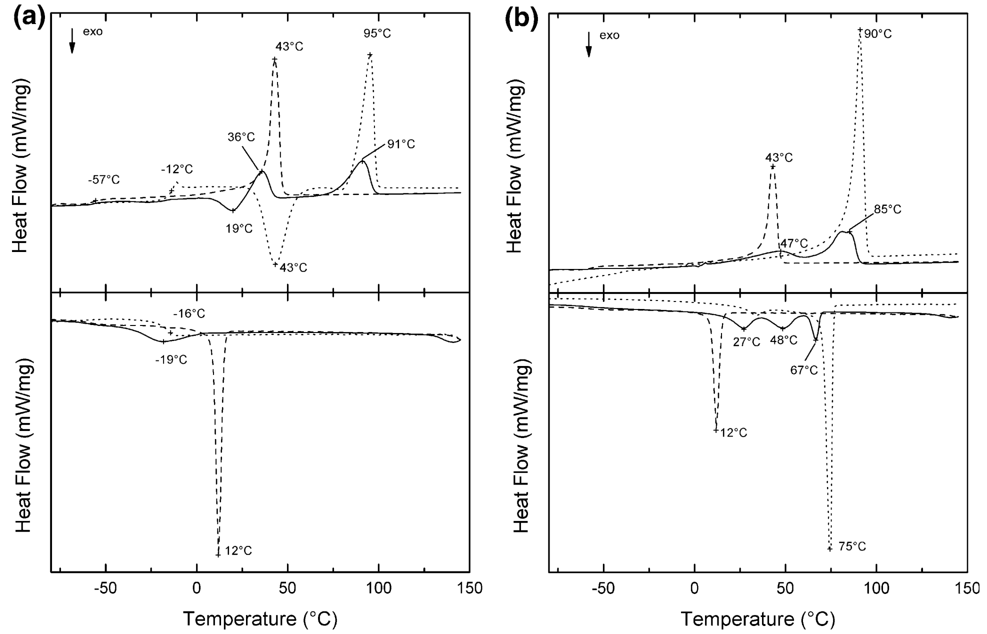


Fig. 3 DSC curves of different multiblock polymer samples second heating run (*upper panel*) and first cooling run (*lower panel*). **a** PDO-MBP (UP) (*dotted line*), PCL-MBP (UP) (*dashed line*), and PCL-*bl*-PDO (UP) (*solid line*); **b** PPD-MBP (UP) (*dotted line*), PCL-MBP (UP) (*dashed line*), and PCL-*bl*-PPD (UP) (*solid line*)

(UP) and PCL-*bl*-PPD (UP) two T_m of the individual components were found. However, in case of PCL-*bl*-PDO (UP) the T_m for the PCL and for the PDO domains were shifted to lower temperatures compared to the respective MBPs due to the disturbance of the crystallization by the PDO segment. In contrast, only one crystallization temperature (T_c) was found in the range of −20 to −7°C. T_gs of both segments were detectable.

In case of PCL-*bl*-PPD (UP) only one T_g was found between −58 and −54°C being attributed to the PCL segment. On the other hand, three T_cs appeared within the range of about 27–31°C, 48–55°C and with about 67°C.

Table 2 Thermal properties of precursor diols and MBCs from DSC measurements: glass transition temperature (T_g), change of heat capacity at T_g (Δc_p), melting temperature (T_m), and melting enthalpy (ΔH_m), and crystallization temperature(s) (T_c)

Polymer-ID[a]	$T_{g,PCL}$ (°C)	$T^{b}_{g,hard}$ (°C)	$T_{m,PCL}$ (°C)	$T^{b}_{m,hard}$ (°C)	$\Delta H_{m,PCL}$ (J g^{-1})	$\Delta H^{b}_{m,hard}$ (J g^{-1})	T_c (°C)
PCL-diol[c]	−64	–	42/46	–	132	–	23
PCL-diol[d]	–	–	49	–	95	–	28
PCL-MBP (UP)[e]	−56	–	43	–	52	–	12
PDO-diol (UP)	–	−28	–	97	–	85	38
PDO-MBP (UP)	–	−15	–	98	–	56	43
PPD-diol (UP)	–	–	–	89	–	168	73
PPD-MBP (UP)	–	–	–	90	–	140	75/34
PCL-*bl*-PDO (UP)	−55	−17	36	91	13	25	−19
PCL-*bl*-PPD (UP)	−56	–	47	81/85	26	42	27/48/67

[a] Identification as in table 1 note a, MBP indicates multiblock polymers containing only one type of polymer segment

[b] The index 'hard' indicates the hard segment, PDO or PPD, respectively

[c] CAPA2205 ($M_n = 2000$ g mol^{-1})

[d] CAPA2304 ($M_n = 3000$ g mol^{-1})

[e] Synthesized from CAPA2205 PCL-diol

Table 3 Mechanical and shape–memory properties of MBCs: young's modulus (E), tensile stress at break (σ_b), elongation at break (ε_b), strain fixity rate and strain recovery rate of the third cycle ($R_f(3)$, $R_r(3)$) from cyclic, thermomechanic measurements applying a lower temperature of 0°C, a higher temperature of 55°C and a programming elongation of 150%

Polymer-ID[a]	25°C			50°C			$R_f(3)$ (%)	$R_r(3)$ (%)
	E (MPa)	σ_b (MPa)	ε_b (%)	E (MPa)	σ_b (MPa)	ε_b (%)		
PCL-*bl*-PDO (UP)	41 ± 6	28.1 ± 1.3	1000 ± 80	13.5 ± 3.0	15.0 ± 1.3	670 ± 50	82	99
PCL-*bl*-PPD (UP)	70 ± 30	15.8 ± 1.1	1100 ± 80	n.d.	n.d.	n.d.	90	96

n.d. Not determined

[a] Identification as in Table 1 note a

This could be an indication for a mixed amorphous phase of PPD and PCL demixing below the $T_{c,PCL}$ and leading to a second PPD crystallization at lower temperatures. The thermal properties of precursor diols as well as MBCs are summarized in Table 2.

3.4 Mechanical and shape–memory properties of the MBCs

The mechanical properties of the MBCs were determined by tensile tests below and above the T_m of the switching segment (25 and 50°C). The upscaled MBCs showed high values for the tensile strength at break at both temperatures, which were very similar to the mechanical properties of the MBCs from SP [7]. However, it has to be pointed out that the different synthesis procedures led to differences in chemical composition since the coupling diisocyanate was replaced. Therefore, influences of the chemical alteration on the mechanical properties can not be excluded.

The shape–memory properties of the MBCs were quantified by cyclic, thermomechanical measurements under stress-control with a programming elongation $\varepsilon_m = 150\%$. R_r of the PCL-*bl*-PDO (UP) showed a good correlation with the same MBC synthesized by SP being higher than 98% in both cases, while R_f of the PCL-*bl*-PDO (UP) was approximately 15% lower than for MBC from SP [7].

In case of PCL-*bl*-PPD (UP) R_r was found in the same range than for the PCL-*bl*-PDO (UP), while PCL-*bl*-PDO (UP) showed higher values for R_f compared to PCL-*bl*-PDO (UP). The mechanical properties and the results from cyclic, thermomechanical measurements are shown in Table 3.

4 Conclusion

Two MBCs with shape–memory capability based on copoly(ether)ester urethanes were synthesized following a newly developed upscaling procedure. In contrast to the previously applied SP, granular products with a grain size of about 3–7 mm were obtained applying UP, which are appropriate for the common processing methods for thermoplastics. It could be shown that the MBCs manufactured in the 1 kg scale could be processed by means of extruding, injection molding, or melt spinning. The shape–memory properties of the MBCs yielded in R_f values between 89 and 97% and R_r values between 95 and 99%. The availability of these multifunctional MBCs is an important step towards their potential application as smart implant materials, which are of special interest for minimally invasive surgery.

Acknowledgment This work was financially supported by the Arbeitsgemeinschaft industrieller Forschungseinrichtungen (grant no. AiF 190ZBG).

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