Electronic supplementary information (ESI)

Star-shaped POSS-polycaprolactone polyurethanes and their shape memory performance

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Experimental setup (CTMs): The thermochamber was used to adjust and control the specimen temperature in the range between 10 to 70 °C. The heating was obtained through two electrical heating elements in the back of the thermochamber. The cooling was done by injecting liquid nitrogen from a tank into the chamber. The liquid nitrogen flow was controlled via a solenoid valve at the nitrogen entrance of the chamber. An electric motor-driven fan behind a baffle provided diffused convection of the thermochamber atmosphere to obtain a uniform temperature distribution. The specimen was shielded by the baffle from direct radiant heat and liquid nitrogen injection. The temperature of the specimen was measured with an Eurotherm thermocouple, which was mounted near the specimen. The tips of the thermocouple were plugged by about 5 mm in depth into rectangular prisms (height: 2 mm, width: 5 mm, length: 12 mm) of the test material in order to create conditions similar to those inside the specimen.

Experimental procedure (CTMs): Hereafter, a detailed description of the free strain recovery experiments (CTM recovery method I) and the fixed-strain constrained stress recovery experiments (CTM recovery method II) is given. In case of the free strain recovery experiments, the test specimen was clamped with an initial gauge length of 10 mm into the grips of the tensile testing machine. Before starting the measurement, the compression stress, which was built up by clamping, was reduced to zero by moving one clamp until the specimen was in its unloaded state (initial strain $\varepsilon_p = 0$). Then the specimen was heated to $T_{\mathrm{high}} = 70$ °C using a heating rate of 18.2

°C min^{-1} (±0.6 °C min^{-1}). T_{high} was lying for all tested SPOSS-PUs above the PCL melting transition. The specimen was held at 70 °C for 5 min before the shape programming process was started. The specimen was elongated to an absolute strain ε_m of 100%, using a strain rate of 0.050 s^{-1} (±0.002 s^{-1}). Strain changes during heating to 70 °C in the first step were included in ε_m. After holding the specimen at that temperature for 5 min, the constrained specimen was cooled to T_{low} = 10 °C (±1 °C), which was below the PCL crystallization transition of all tested SPOSS-PUs, using a cooling rate of 16.6 °C min^{-1} (±3.4 °C min^{-1}). The specimen was kept under constant strain for another 5 min. Unloading the specimen with a rate of 5.0 N min^{-1} (±0.4 N min^{-1}), adjacent holding for 5 min and measuring of the strain ε_u of the new unconstrained temporary shape completed the shape programming process. Shape recovery was initiated by reheating the specimen to 70 °C with the abovementioned heating rate. The shape (free strain) recovery onset temperature was defined by the value of the tangent line through the inversion point of the shape recovery curve at the foregoing temporary shape ε_u in the strain-time diagram. The corresponding temperature was taken as onset shape (free strain) recovery temperature $T_{r,onl}(N)$. The residual strain associated with the recovered permanent shape ε_p was measured after 5 min at T_{high}. This step completed the entire first thermo-mechanical cycle (N = 1). Subsequently, four further cycles (N = 2–5) were run, each starting with the elongation of the specimen to ε_m. Every complete (5 cycle) test series took about 180 min.

In case of the fixed-strain constrained stress recovery experiments (CTM recovery method II), a detailed analysis of the specimen behavior during the abovementioned programming process was made. In the deformation step (stretching to ε_m), attention was paid to changes in Young's modulus E' and loading stress $\sigma_l(N)$, both were determined at 70 °C. After stress relaxation, large parts of the applied tensile stress were frozen through specimen cooling to T_{low}. The temperature,

at which the specimen started to build up thermal stress, was termed "thermal stress onset temperature" $T_{t,on}(N)$. Keeping the specimen for 5 min under constant strain at T_{low} resulted in the development of thermal stress, whose maximum value $\sigma_{t,max}(N)$ was determined. The stress was completely unloaded at T_{low} and the specimen was kept at that temperature for another 5 min. In the next step the constrained specimen was heated from 10 to 70 °C. Before the shape (stress) recovery effect was initiated, some thermal expansion of the specimen took place, leading to the development of a minimum stress $\sigma_{t,min}(N)$. Similar to the strategy with which the onset shape (free strain) recovery temperature was determined, $T_{r,onII}(N)$ was defined as that temperature in the stress-time diagram, where the stress value of the tangent line through the inversion point of the stress recovery curve was zero. Beyond this, the maximum recoverable stress $\sigma_{r,max}(N)$ was recorded.

Determination of the error limits for thermo-mechanical parameters of SPOSS-PUs: For cycle $N = 1$, the errors of all parameters were determined using statistical methods. They do not include systematical uncertainties. In case of $\sigma_l(N)$, $R_f(N)$, $R_r(N)$ and $R_{r,tot}(N)$ the errors were given by the standard deviation of three identical measurements of SPOSS-PU 200 and were applied to the measurement data of SPOSS-PU 160, SPOSS-PU 240 and SPOSS-PU 400, respectively. For $\sigma_{t,max}(N)$, $\sigma_{t,min}(N)$ and $\sigma_{r,max}(N)$ the statistical distribution of values around the mean value was given. Similarly, the errors for $T_{r,onI}(N)$ and $T_{r,onII}(N)$ were determined by the statistical distribution of values along a linearly fitted temperature increase (at constant heating rate).

The error of $T_{t,on}(N)$ was determined by the projection of the stress error limits around $\sigma_{t,min}(N)$ onto the corresponding temperature values. The error limits of $E'(N=1)$ were estimated from the

width of the statistical distribution of the stress-strain derivative. For all (N = 2-5)-averaged parameters, the root mean square deviation was given.