Supplementary information

Tailoring the morphology and melting points of segmented thermoplastic polyurethanes by self-nucleation

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Figure S1. *Self-nucleation experiments. Cooling and subsequent heating DSC traces*

**PUest33**

*Cooling scans from indicated $T_s$ values*

[Graph of cooling scans showing heat flow against temperature for various $T_s$ values.]

*Subsequent heating scans*

[Graph of subsequent heating scans showing heat flow against temperature for various $T_s$ values.]
PUeth30

Cooling scans from indicated $T_s$ values:

Subsequent heating scans:
**PUeth43**

*Cooling scans from indicated $T_i$ values:*

![Cooling scans diagram](image)

*Subsequent heating scans:*

![Heating scans diagram](image)
Figure S2. Spherulitic texture of a “standard” morphology as observed by PLOM.

Figure S2. a) Thermal program for the morphological analysis shown in (b). b) DSC curve along the polarized light optical micrographs at different temperatures of PUeth30. The DSC curve was recorded at 20 °C·min\(^{-1}\) while the images were acquired during a heating program of 10 °C·min\(^{-1}\). Scale bars are of 88 \(\mu\)m.
Figure S3. Impact of self-nucleation/crystallization on TPU's morphology as studied by PLOM.

Figure S3a. Influence of different thermal treatments onto the morphology of PUest33. a) Spherulites obtained after 50 min crystallization at 160 °C after cooling from DI. b) Morphology obtained after direct cooling from DI at 20 °C·min⁻¹. C) High nucleation density exhibited after 5 min crystallization at 160 °C after cooling from DII (T_s = 192 °C). Scale bars are of 88 μm.
Figure S3b. Influence of different thermal treatments onto the morphology of PUeth30. a) Spherulites obtained after 190 min crystallization at 160 °C after cooling from $D_I$. b) Morphology obtained after direct cooling from $D_I$ at 20 °C·min$^{-1}$. C) High nucleation density exhibited after 5 min crystallization at 160 °C after cooling from $D_{II}$ ($T_s = 192$ °C). Scale bars are of 88 μm.
Figure S3c. Influence of different thermal treatments onto the morphology of PUeth43. a) Spherulites obtained after 5 min crystallization at 160 °C after cooling from DI. b) Morphology obtained after direct cooling from DI at 20 °C·min⁻¹. C) High nucleation density exhibited after 5 min crystallization at 160 °C after cooling from DII (Tₛ = 210 °C). Scale bars are of 88 μm.
Figure S3d. Influence of different thermal treatments onto the morphology of PUeth43. a) Spherulites obtained after 53 min crystallization at 180 °C after cooling from DI. b) Morphology obtained after direct cooling from DI at 20 °C·min⁻¹. C) High nucleation density exhibited after 17 min crystallization at 180 °C after cooling from DII (Ts = 210 °C). Scale bars are of 88 μm.
Figure S4. *Domain borders as extracted from DSC self-nucleation analysis.*

Figure S4. Temperature domain ranges shorted according to their SN behavior for each of the studied TPUs and plotted in the same temperature scale.
Figure S5. Impact of cooling rate on self-nucleated samples at different domains ranges.

Figure S5. Influence of cooling rate on morphology. Subsequent heating scans after cooling at the indicated heating rates (°C·min$^{-1}$) from different temperatures at DI, DII and DIII of a) PUest33, and b) PUeth43. *Indicates a ballistic cooling rate of ≈ 160 °C·min$^{-1}$. 
Figure S6. In-situ SAXS curves during heating from $T = 40 \, ^\circ\text{C}$ to the molten state for (a) PUest33, (b) PUeth30 and (c) PUeth43 being cooled with 5 $^\circ\text{C} \cdot \text{min}^{-1}$ after SN (first column), cooled with 100 $^\circ\text{C} \cdot \text{min}^{-1}$ after SN (second column) or annealed at 100 $^\circ\text{C}$ for 20 h after injection molding (third column). For clarity only selected data are presented. The $T_c$ temperature employed for SN was 192 $^\circ\text{C}$ (for PUest33 and PUeth30) and 210 $^\circ\text{C}$ for PUeth43.