Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Effect of separation of blocks on crystallization kinetics and phase composition of poly(butylene adipate) in multi-block thermoplastic polyurethanes

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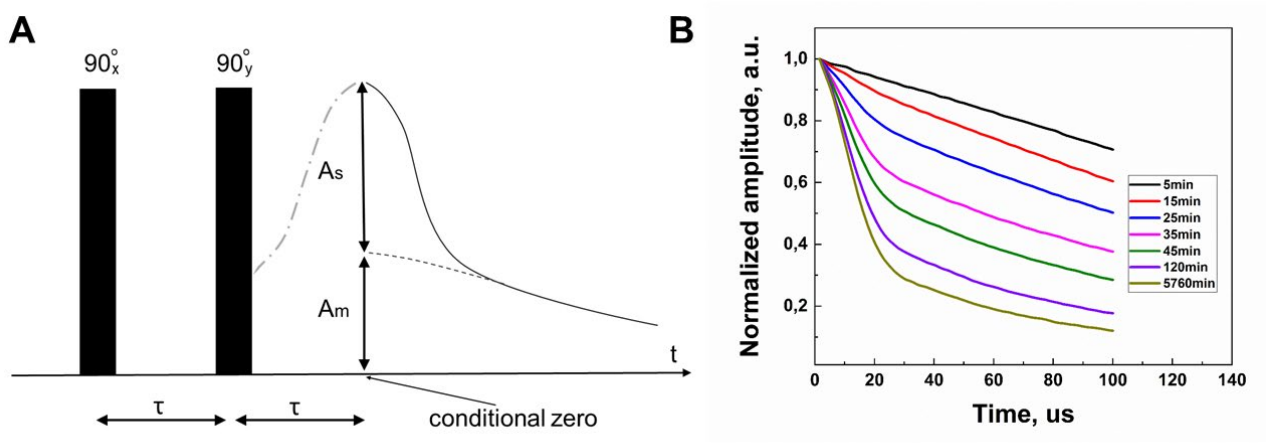

Fig. S1 Pulse sequence diagram of the SE signal (A) and normalized SE decays of TPU-IPDI recorded in crystallization at 20°C after cooling from 150 °C (B).

The solid-state echo decay pulse train consists of a 90° at RT pulse in the x direction followed by a 90° pulse in the y direction after a delay time τ. Continuously increasing τ and registering the maximum of the echo signal by 2τ, at the top of which a conditional zero is established, the decay of the transverse magnetization is recorded.

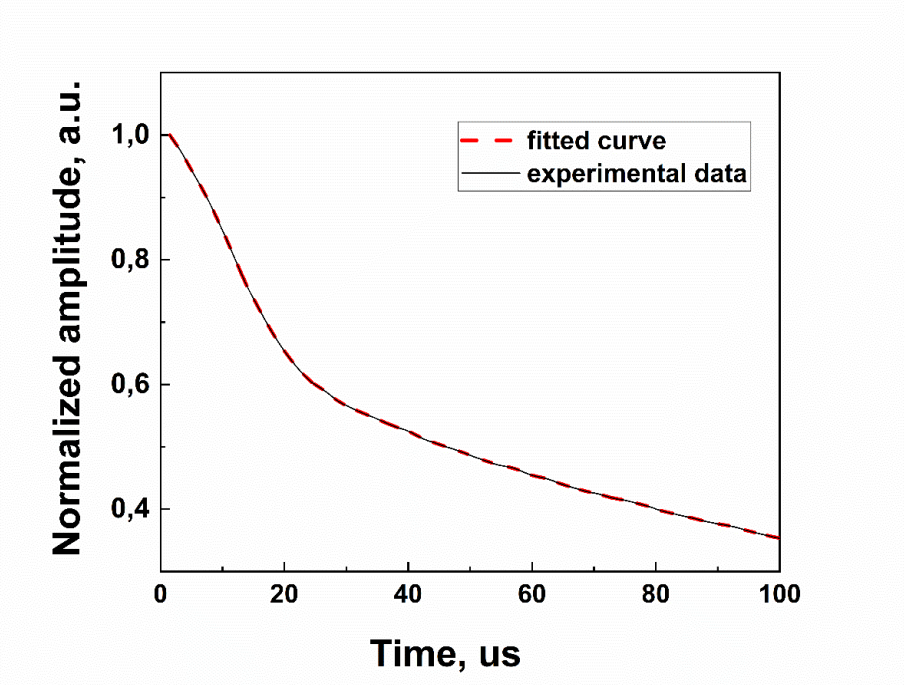

Fig. S2 Experimental and fitted dependence of the Free Induction Decays (FID) of a two-step damping form Gaussian to exponential due to differences in the segmental mobility of the rigid and amorphous phases.

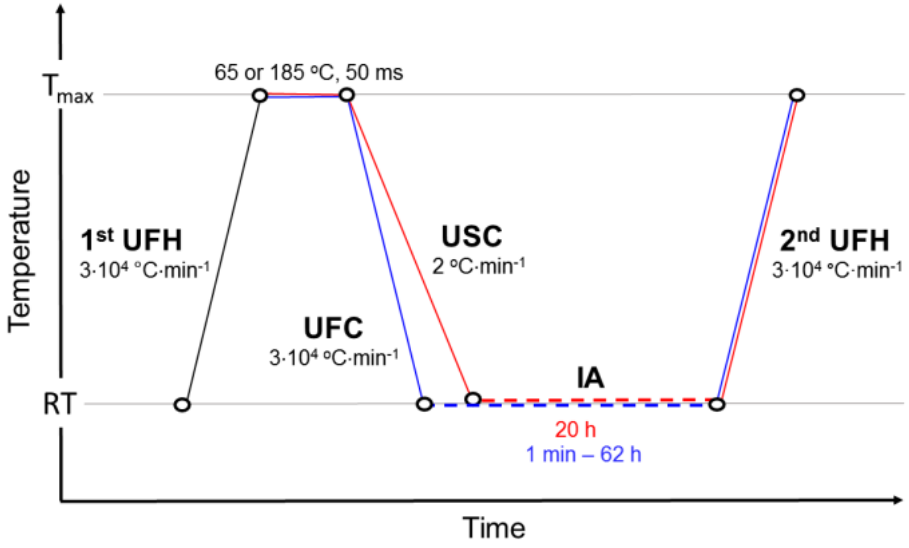

Fig. S3 Temperature programs for nanocalorimetric measurements: Program 1 (black line), Program 2 (red lines) and Program 3 (blue lines).

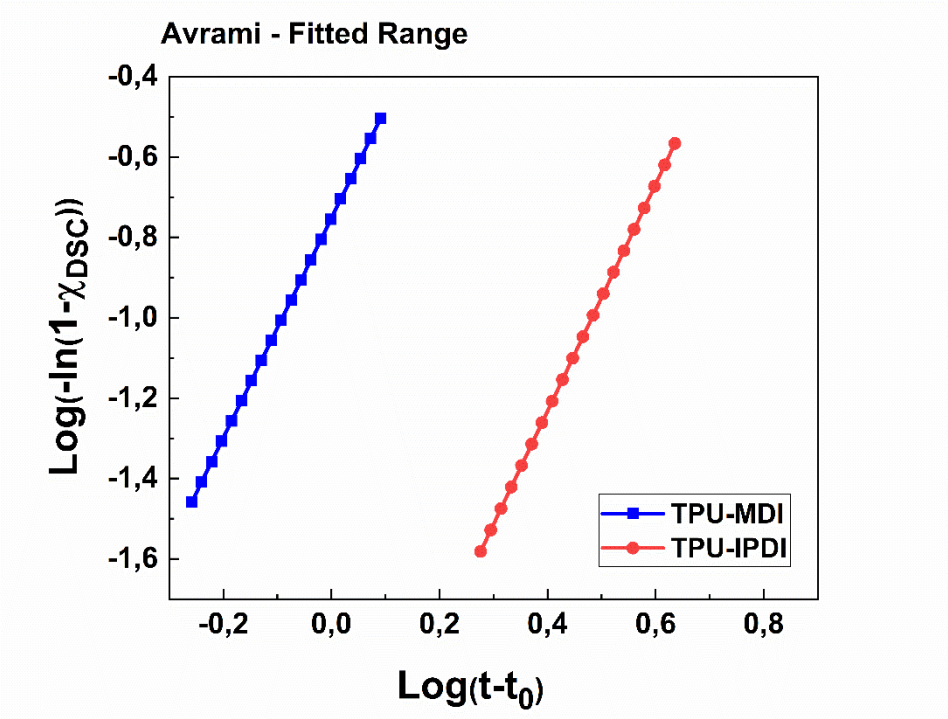

Fig. S4 Time dependence of χ_{DSC} in Avrami coordinates for TPU-MDI (blue curve) and TPU-IPDI (red curve).

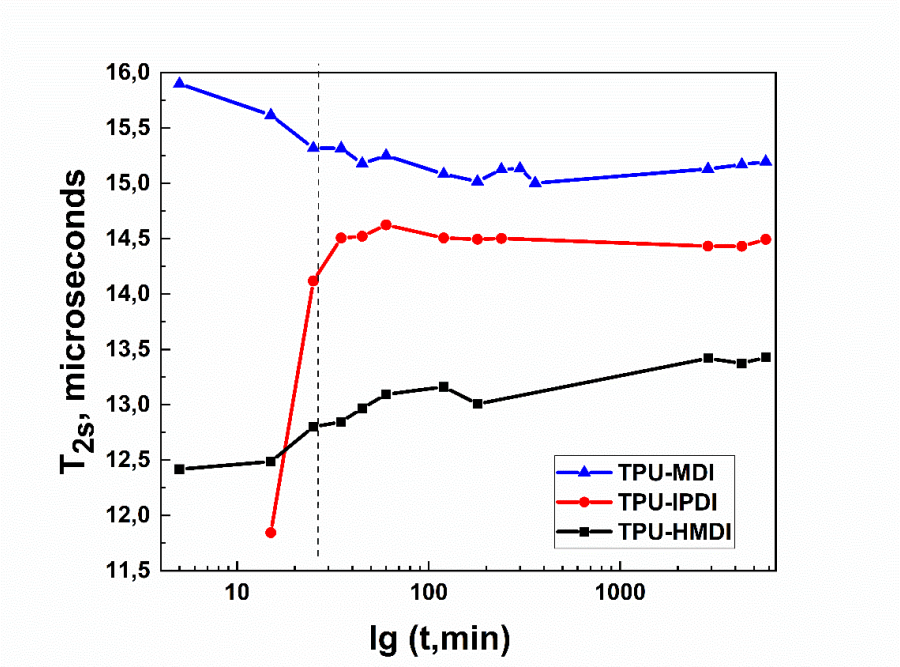

Fig. S5 Changes in the spin-spin relaxation time T_{2s} during crystallization at 20 °C after cooling from 150 °C.

Normally, the general trend in relaxation time of a rigid fraction with cooling and crystallizing should show the decrease of T_{2S}. For the sample TPU-HMDI we observe definitely reversed behavior that can be explained by more intensive magnetization exchange between crystals and amorphous regions due to presence of in intermediate mesophase.

Table S1 Main frequencies and assignments of FTIR bands to crystal phases of PBA oligodiol.

Main assignment	Wavenumber, cm^{-1}	Phase	Wavenumber, cm^{-1}	Phase	Wavenumber, cm^{-1}	Phase
	20 °C/min		2 °C/min		storage at RT	
ɣ CH_2	911	β	908	α	908	α
ɣ CH_2	930	β	-	α	-	α
ɣ CH_2	958	β	957	α	957	α
σ_s CH_2	1371	β	1368	α	1368	α
σ_{as} CH_2	1401	β	1398	α	1398	α
δ_s CH_2	1416	β	1418	α	1418	α
δ_{as} CH_2	1464	β	1461	α	1461	α
υ_{as} C-O-C	1258	β	1257	α	1257	α
υ_s C-O	1162	β	1160	α	1160	α

Thus, it has been established that upon 20 °C/min cooling, the pure β-form crystallizes, while upon 2 °C/min cooling, the pure α-form crystallizes («fresh»). Storage («old») of PBA at RT leads to the formation of the α-phase.

Table S2 Main frequencies and assignments of FTIR bands to crystal phases of PBA in TPUs.

Main assignment	wavenumber, cm^{-1}	phase	wavenumber, cm^{-1}	phase	wavenumber, cm^{-1}	phase
	TPU-MDI		TPU-IPDI		TPU-HMDI	
2 °C/min after 65 °C						
ɣ CH_2	910	α+β	910	α+β	909	α+β
ɣ CH_2	930	α+β	930	-	930	α+β
ɣCH_2	959	β	960	β	959	β
σ_s CH_2	1369	α+β	1369	α+β	1368	α
σ_{as} CH_2	1397	α	1398	α	1396	α
δ_s CH_2	1415	α+β	1418	α	1417	α
δ_{as} CH_2	1462	α	1461	α	1463	α+β
20 °C/min after 150 °C						
ɣ CH_2	910	α+β	910	α+β	910	α+β
ɣ CH_2	930	α+β	930	α+β	930	-
ɣ CH_2	959	β	958	β	958	β
σ_s CH_2	1369	α+β	1368	α	1368	α
σ_{as} CH_2	1397	α	1398	α	1396	α
δ_s CH_2	1414	β	1418	α	1417	α
δ_{as} CH_2	1461	α+β	1461	α	1461	α
20 °C/min after 185 °C						
ɣ CH_2	-	-	-	-	909	α+β
ɣ CH_2	-	-	-	-	930	α+β
ɣ CH_2	-	-	-	-	959	β
σ_s CH_2	-	-	-	-	1369	α+β
σ_{as} CH_2	-	-	-	-	1398	α+β
δ_s CH_2	-	-	-	-	1417	α

γ CH_2	-	-	-	-	1463	β

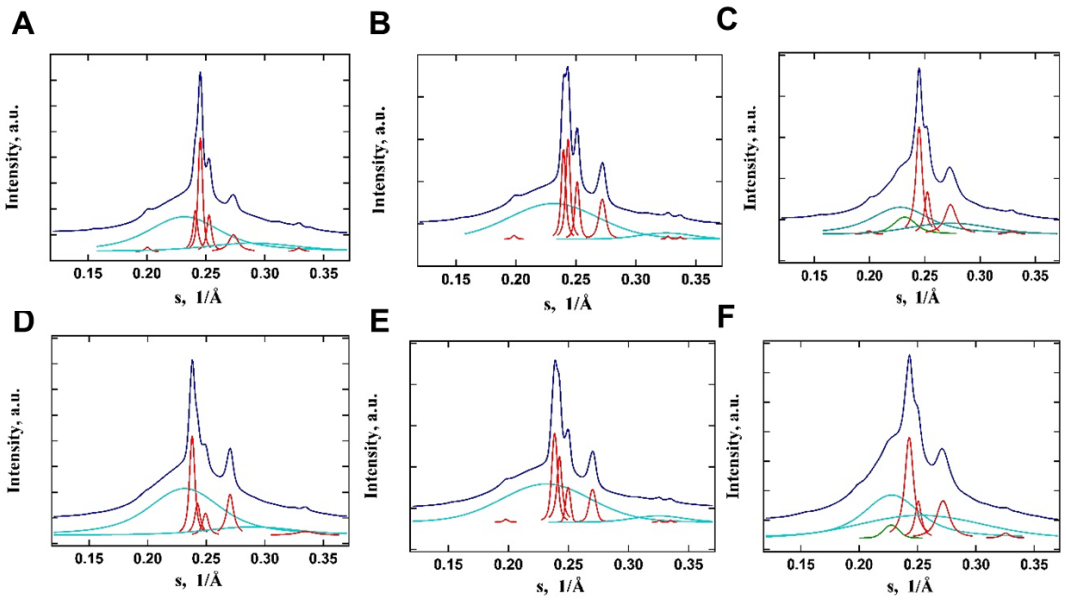

Fig. S6 Fitting with set of Gaussians of WAXS patterns of TPU-MDI (A, D), TPU-IPDI (B, E) and TPU-HMDI (C, F) after long storage (A-C) and after crystallization from 150 °C for 20 hours at RT (D, F). Red, cyan and green curves indicate crystalline, amorphous and mesophase peaks, respectively.

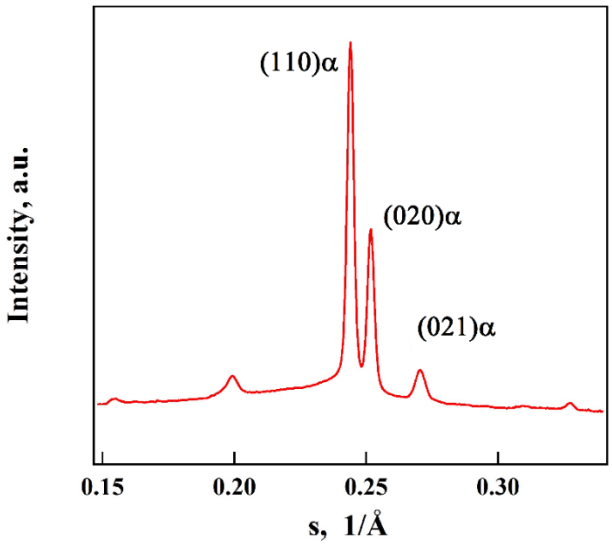

Fig. S7 WAXS diffractogram of PBA oligodiol (only α modification).

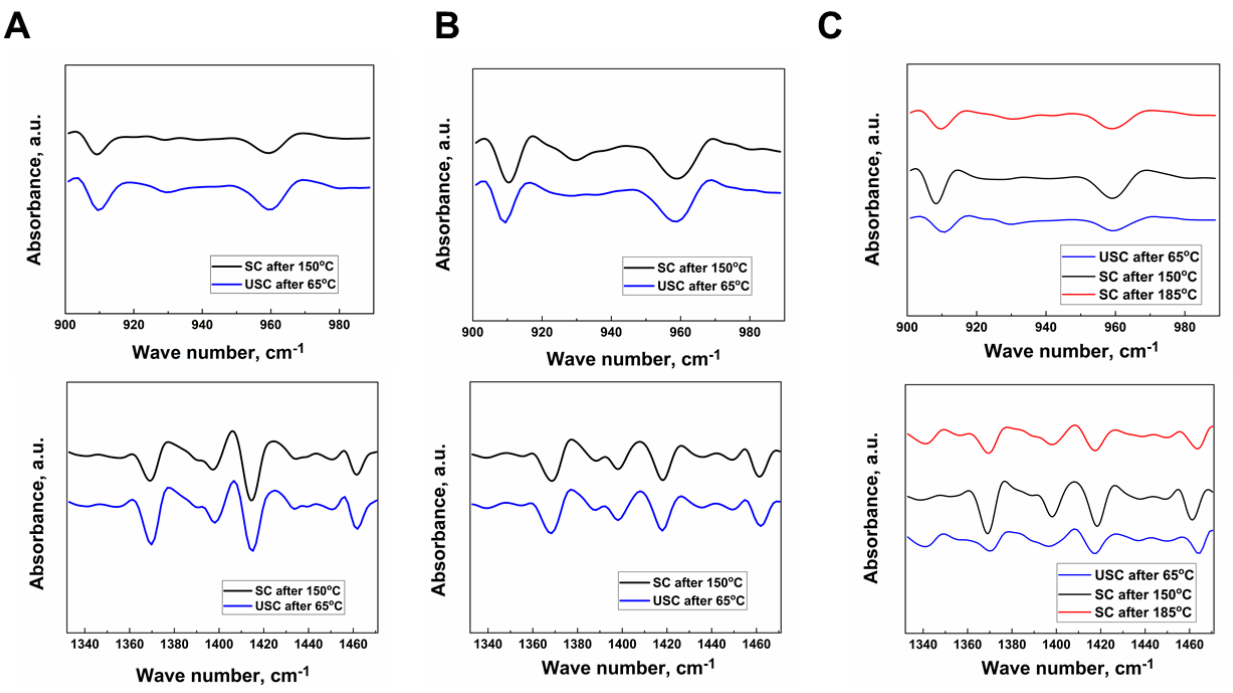

Fig. S8 Second derivatives of the IR spectra of the TPU series for TPU-MDI (A), TPU-IPDI (B) and TPU-HMDI (C), differing in the hard block structure and crystallized under different cooling conditions.

Table S3 Effect of crystallization conditions on the phase composition of PBA for different TPUs taken at the same time interval after crystallization

Sample preparation conditions	Cooling	Rate, °C/min	T_{max} heat, °C	FSC*	FTIR	WAXS
PBA						
stored at RT	-			α**	α	α
recrystallized at RT	UFC	30000	185	β	-	-
	SC	20	65	-	β	-
	USC	2	65	-	α	-
TPU-MDI						
stored at RT	-			α+β**	α+β	α+β
recrystallized at RT	UFC	30000	185	α	-	-
	USC	2	185	α+β	-	-
	SC	20	150	-	α+β	α+β
	USC	2	65	-	α+β	-
TPU-IPDI						
stored at RT	-			α+β**	α+β	α+β
recrystallized at RT	UFC	30000	185	α	-	-
	USC	2	185	α+β	-	-
	SC	20	150	-	α+β	α+β
	USC	2	65	-	α+β	-

TPU-HMDI						
stored at RT	-			α**	α	α
recrystallized at RT	UFC	30000	185	α+β	-	-
	SC	20	185	-	α+β	-
	USC	2	185	α	-	-
	SC	20	150	-	α	α
	UFC	30000	65	α	-	-
	USC	2	65	α	>α	-

*UFH/UFC – ultra-fast heating/cooling with rate of 30 000 °C/min

**heating of the initial sample from RT to 185 °C

SC – slow cooling with rate of 20 °C/min

USC – ultra-slow cooling with rate of 2 °C/min

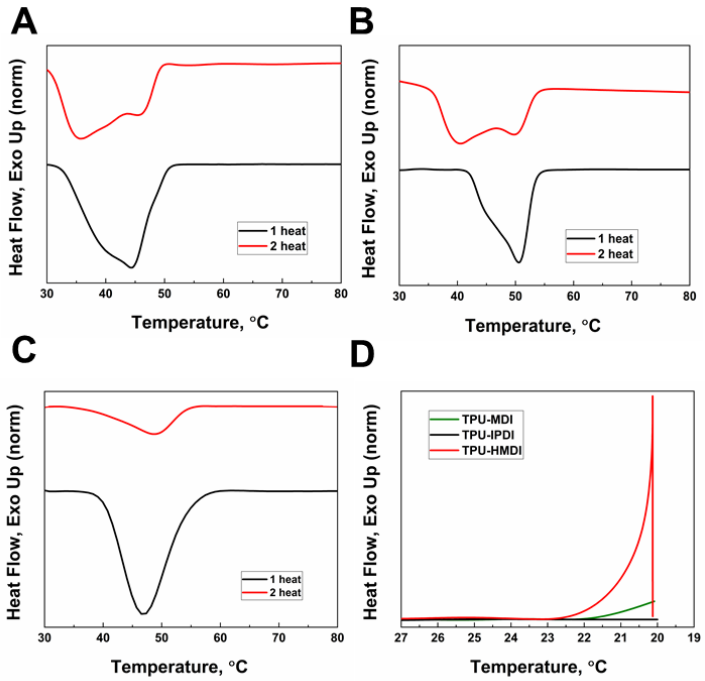

Fig. S9 DSC heating curves up to 150 °C of the initial films (1st heating, black curves) and after 30-min crystallization at 20 °C (2nd heating, red curves) for TPU-MDI (A), TPU-IPDI (B), TPU-HMDI (C) and 1st cooling curves (D).

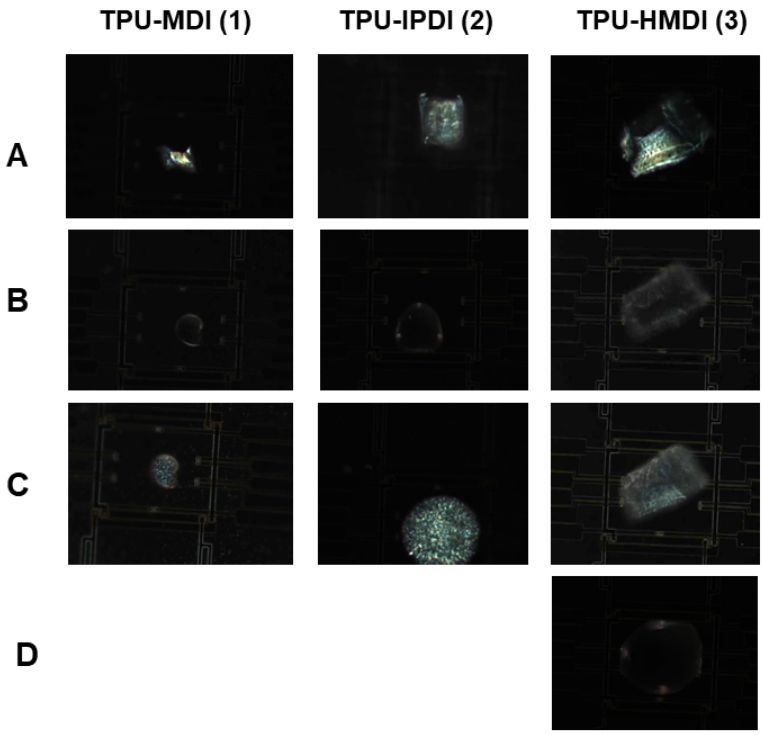

Fig. S10 Micrographs of TPU microparticles in polarized light.

For TPU-IPDI and TPU-MDI: particle linear sizes are about 75x75 and 40x30 microns, respectively. Before the 1st heating (A); after the 1st heating, at 185 °C (B); after 20 hour annealing at RT, right before the 2nd heating (C). For TPU-HMDI: particle linear sizes are about 100x70 microns. Before the 1st heating (A); after the 1st heating, at 65 °C (B); after 20 hour annealing at RT, just before the 2nd heating to 185 °C (C); just after the 2nd heating, at 185 °C (D).