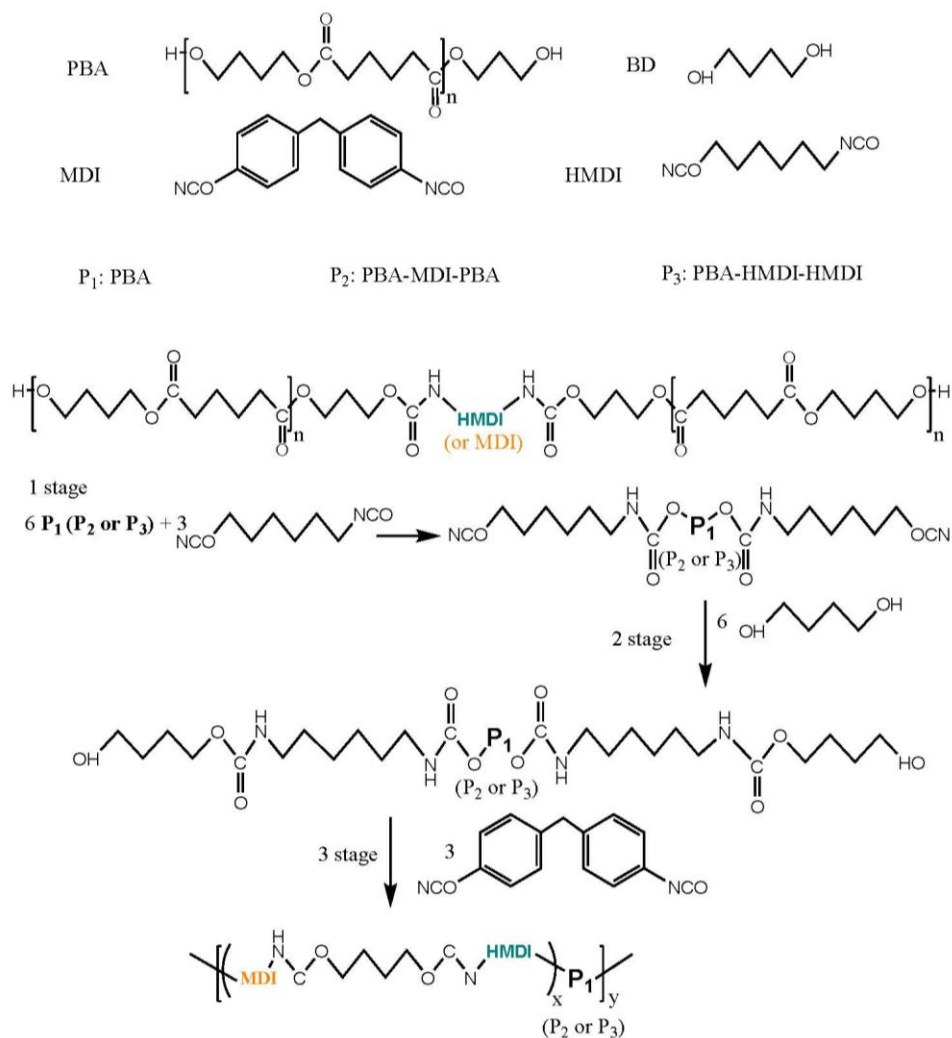


Table S1. Stoichiometry of the designed TPUs

	PBA diols (mmol)	HMDI ^a (mmol)	HMDI ^b (mmol)	MDI ^b (mmol)	BD ^b (mmol)	HS, %
TPU(PBA)	6	0	0	12	6	35
TPU(PBA-MDI)	6	0	3	9	6	35
TPU(PBA-HMDI)	6	3	0	9	6	35

^aHMDI is used to prepare macrodiols.^bHMDI is used to prepare hard block.**Scheme S1.** The reaction scheme of the designed TPUs.

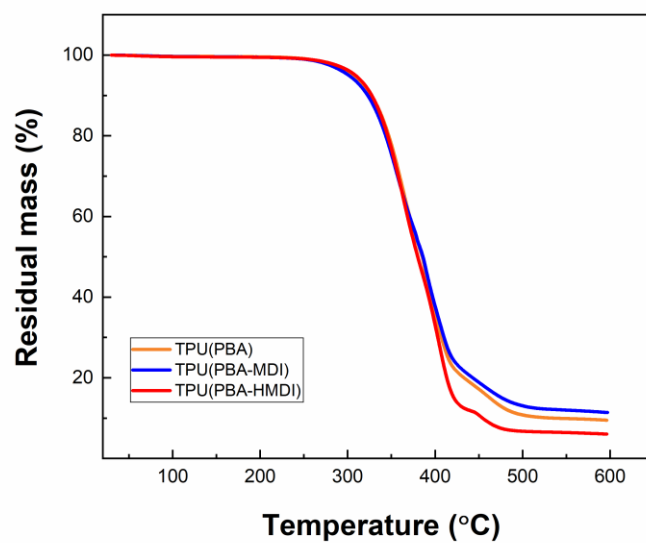


Figure S1. TGA curves for the TPU samples measured at a rate of 10 °C/min in nitrogen atmosphere.

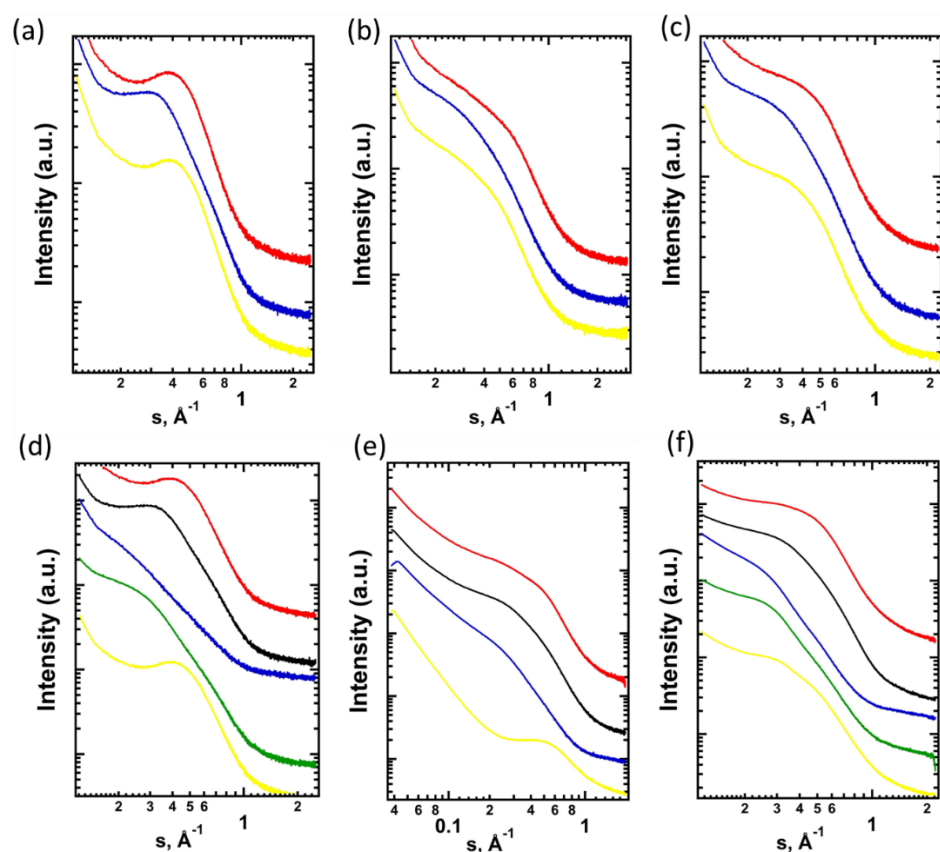


Figure S2. SAXS curves of TPU(PBA-HMDI) (a, d), TPU(PBA) (b, e), TPU(PBA-MDI) (c,f): initial (red), after SS melting (black), at maximum temperature (blue), immediately after cooling (green) and after isothermal crystallization (yellow): $T_m = 80\text{ °C}$ (a,b,c) and $T_m = 180\text{ °C}$ (d,e,f).

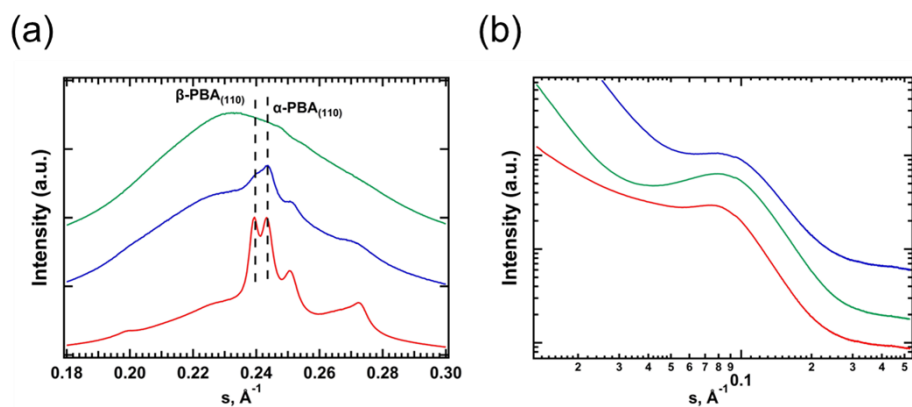


Figure S3. WAXS (a) and SAXS (b) curves for TPUs after cooling from 230°C and crystallization for 1 week at RT: TPU(PBA) (green), TPU(PBA-MDI) (blue), TPU(PBA-HMDI) (red).

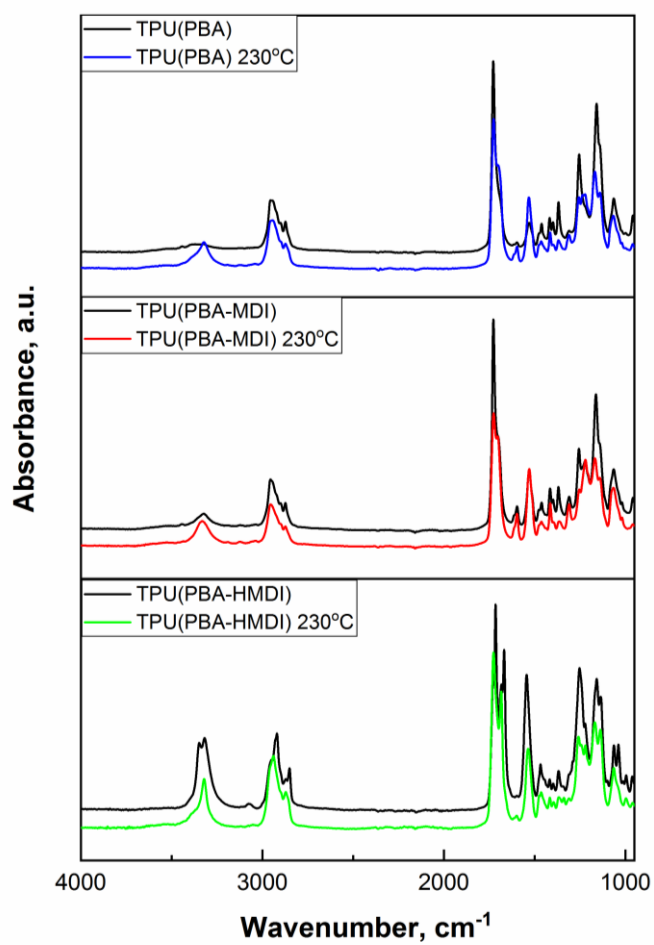


Figure S4. IR spectra for the native samples (black curve) and samples crystallized after heating to 230 °C (color curves).

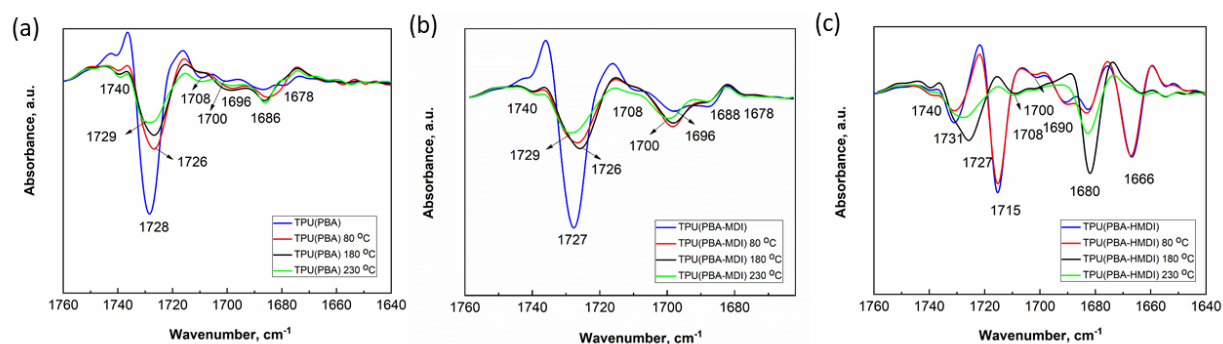


Figure S5. The second derivatives IR spectra TPU(PBA) (a), TPU(PBA-MDI) (b) and TPU(PBA-HMDI) (c) native samples (blue lines) and crystallized after 80°C (red lines), 180°C (black lines) and 230 °C (green lines).