

Figure S1 Gel permeation chromatogram elution curve overlay of PU-PCL50-AO heated at various temperatures for various times showing different stages of polymer formation; note that at the lower temperatures the curves are clearly bimodal reflecting considerable amounts of low molecular species; the area highlighted in red shows the disappearance of MDI-AO

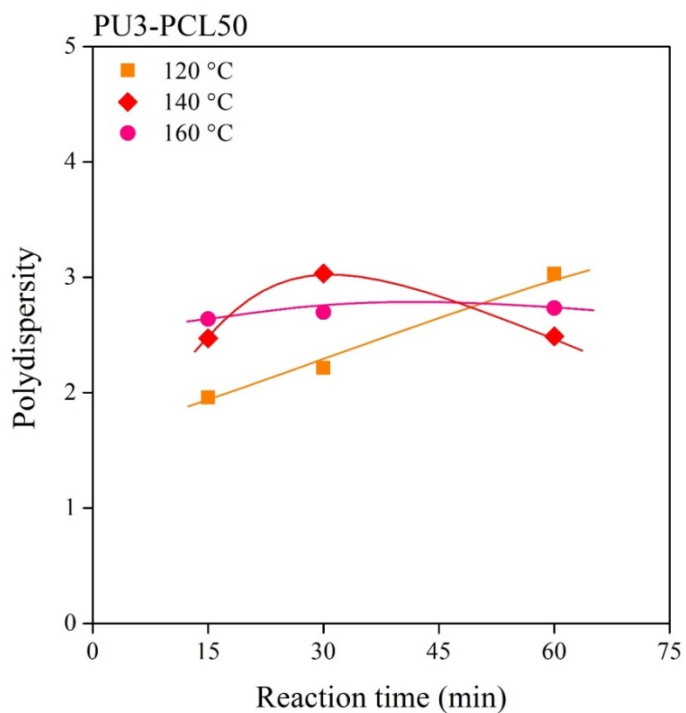
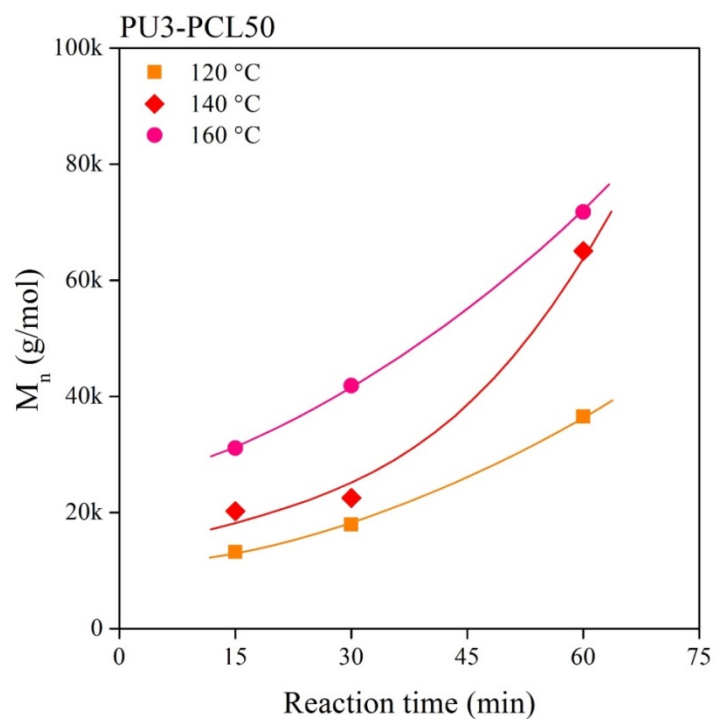


Figure S2 **a)** shows the number average molecular weight (M_n) of PU-PCL50-AO as a function of both reaction time and temperature. It is evident from the plot that the molecular weight increases only slightly as a function of time below 120°C. The highest molecular weights were obtained for 60 min at 140°C and 60 min at 160°C; **b)** illustrates the PDI differences observed with reaction time and temperature

Sample: PU-PCL50 140C 60min- Size:
5.5716 x 8.6300 x 0.1200 mm Method:
Strain Sweep

DMA

File: PU-PCL50-AO 5percSnOct2 140C 60min-2 ...
Operator: Balázs
Run Date: 29-Apr-2015 14:18
Instrument: DMA Q800 V20.24 Build 43

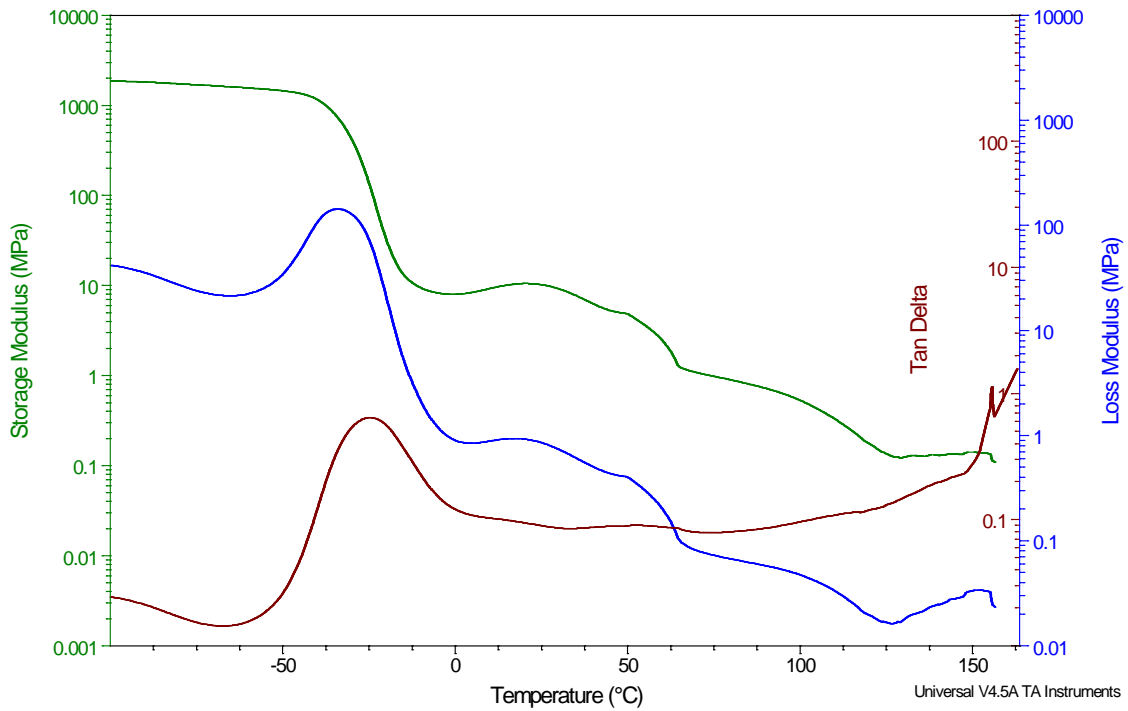


Figure S3 Dynamic mechanical analysis (DMA) data for PU-PCL50-AO polymerized at 140°C for 60 minutes; the low temperature loss peak signifies T_g of the soft phase ; the increase in storage modulus above 0°C is associated with modest cold crystallization within the PCL phase; crystallinity in the this is followed by melting of PCL crystallinity at ~ 50°C; The event at ~125°C is probably due to the disruption of inter-urethane hydrogen bonds

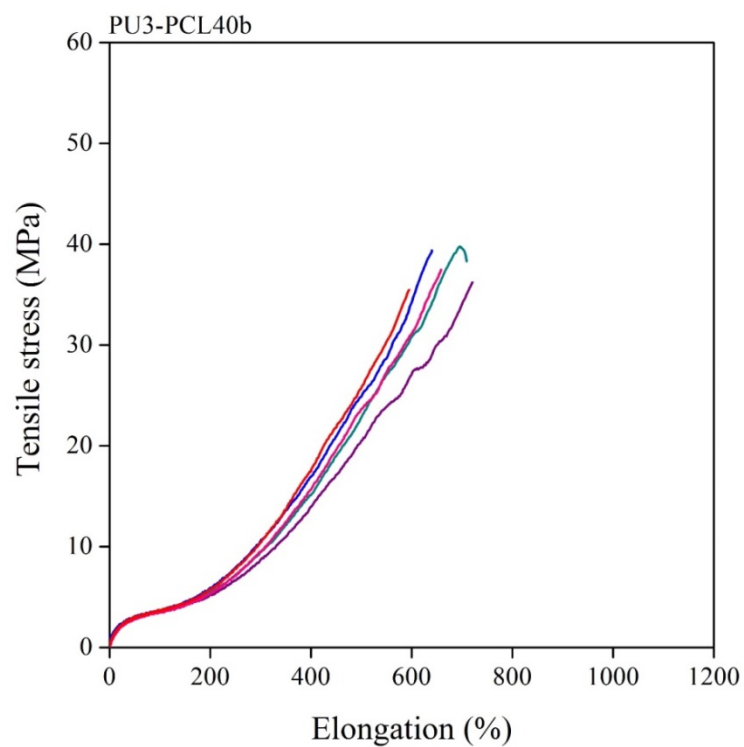


Figure S4 Tensile stress-elongation data for unblocked PU-PCL40 PU film polymerized at 140°C for 60 min; Film composition is 40 % PCL based on -OH content; results were obtained for 5 samples at room temperature, extension rate 50 mm/min