

Stretchable and Degradable Semiconducting Block Copolymers

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Chemical Synthesis

Table S1. Molecular characterization of synthesized PDPPs, PCL, and BCPs.

	Entry	PDPP	PCL (wt%)		Yield (%)	M_n^b (kg/mol)	M_w^b (kg/mol)	M_p^b (kg/mol)	PDI ^b
			Input	In polymer ^a					
Prepolymer	T-0	-	-	-	92	19.1 (26.2)	61.2 (84.4)	44.4 (46.8)	3.2 (3.2)
	TT-0	-	-	-	98	24.2 (31.3)	79.9 (120.7)	40.7 (42.6)	3.3 (3.9)
	PCL	-	-	-	93	25.1	34.8	36.4	1.4
BCP	T-25	T-0	25	30	95	21.8 (22.0)	64.2 (82.0)	54.5 (59.8)	2.9 (3.7)
	T-50	T-0	50	53	95	25.7 (32.7)	81.9 (124.2)	65.9 (73.8)	3.2 (3.8)
	T-75	T-0	75	78	89	22.9 (27.7)	79.2 (122.0)	73.1 (73.8)	3.5 (4.4)
	T-90	T-0	90	91	96	28.4 (34.4)	65.8 (102.5)	37.6 (32.7)	2.9 (3.0)
	TT-25	TT-0	25	27	99	29.8 (41.2)	95.3 (163.8)	54.9 (65.7)	3.2 (4.0)
	TT-50	TT-0	50	55	99	25.9 (40.0)	106.2 (180.2)	78.4 (96.8)	4.1 (4.5)
	TT-75	TT-0	75	73	95	28.8 (46.2)	118.2 (257.9)	68.6 (87.5)	4.1 (5.6)
	TT-90	TT-0	90	91	98	28.7 (40.1)	94.4 (165.2)	40.7 (60.3)	3.3 (4.1)
	Blend	T-blend-50	T-0	50	-	18.2 (22.4)	44.7 (67.7)	36.4 (29.5)	2.5 (3.0)

a Determined by ¹H NMR spectroscopy; **b** Determined by GPC relative to PS standards using a refractive index concentration detector or a UV detector at 800 nm (shown in parentheses).

Mechanical Properties Using the “Film-on-Water” (FOW) Technique

Table S2. Mechanical properties of synthesized prepolymers and BCPs. Thin films (5 mm x 1 cm, 100-200 nm thick) on PEDOT:PSS were scored using razors and floated onto the surface of the water from a glass slide.

Entry	Elongation at break (%)		Toughness (kJ/m ³)		Young's modulus (MPa)	
	Ave	SD	Ave	SD	Ave	SD
T-0	13	1	0.78	0.09	239	22
T-25	15	2	0.79	0.11	173	9
T-50	87	6	6.89	0.83	200	29
T-75	208	25	17.5	3.8	196	26
TT-0	3	1	0.14	0.03	515	21
TT-50	80	21	8.08	1.62	247	5

*Ave: Average of 3 distinct measurements; SD: Standard deviation of 3 distinct measurements

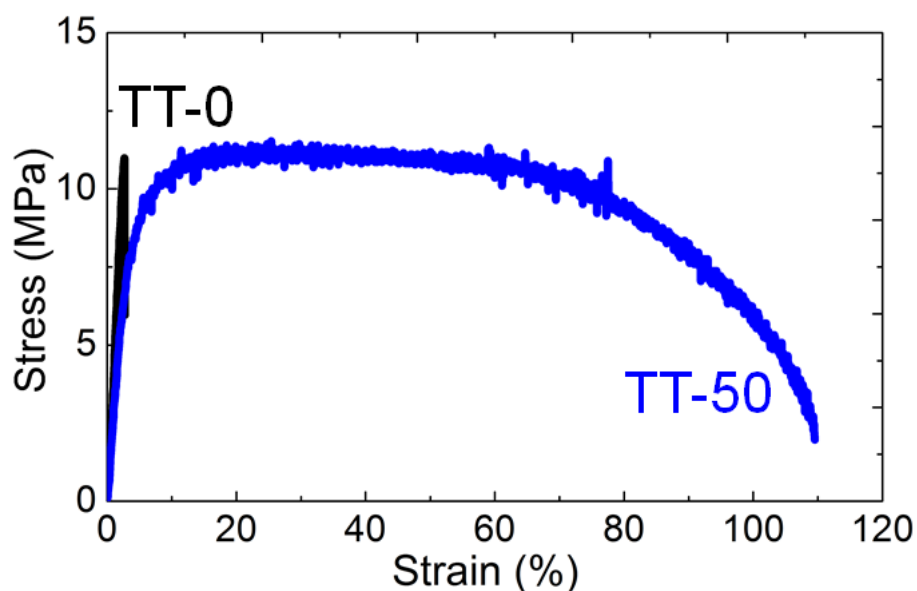


Figure S1. Stress-strain curves of TT-0 and T-50 obtained from the FOW technique

Surface Morphology

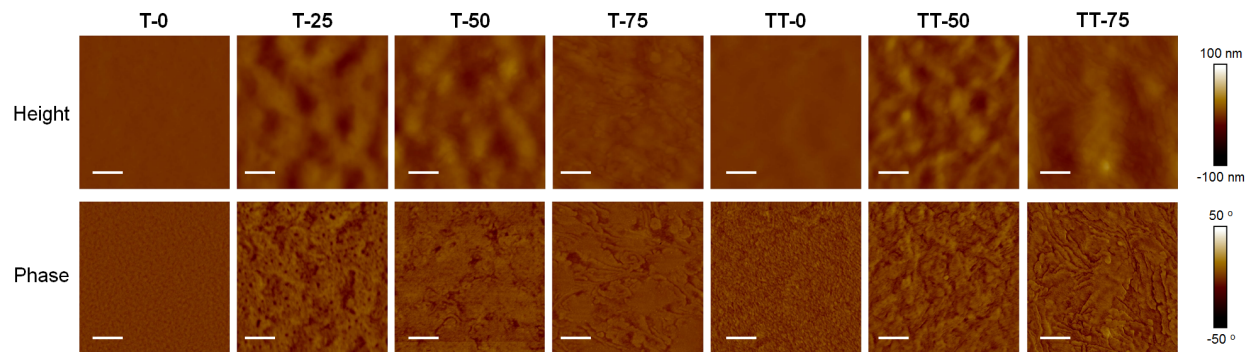


Figure S2. AFM height and phase images of **BCP-Ts**. The scale bar is 300 nm.

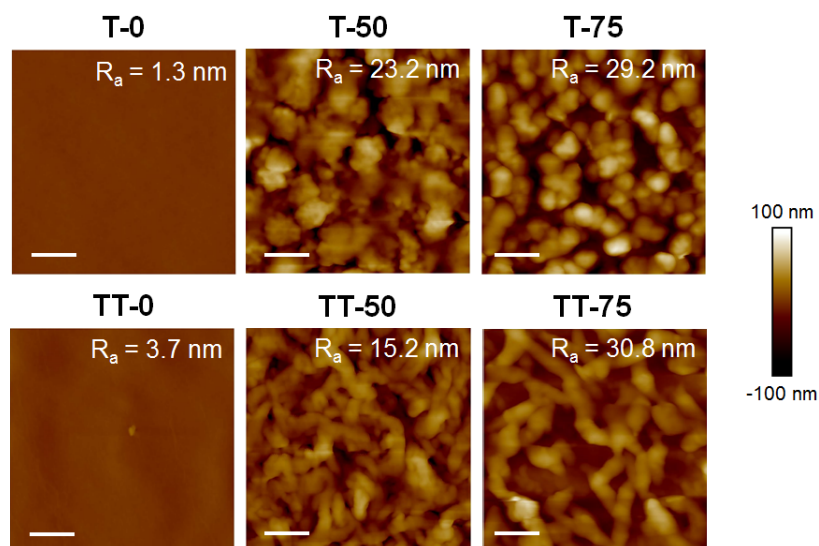


Figure S3. AFM height images of BCP thin films after 3 days of exposure to a basic solution (0.5 M sodium hydroxide solution in water/methanol = 60/40 (volume/volume)%). R_a is the average roughness of the scanned area, scale bar, 300 nm.

Cracking Behavior

We examined cracking behavior of thin film using a linear actuator and optical microscopy. Spin-coated thin films were removed from plasma-treated glass substrates and floated on a water surface. The films on water were transferred to stretchable PDMS (Sylgard 184, Dow Corning) substrates. PDMS was prepared according to the manufacturer's instructions at a ratio of 10:1 (base:crosslinker) and cured at room temperature for 36 to 48 h prior to use for mechanical testing.



Figure S4. Schematic illustration of the procedure used to observe cracking behavior of thin films.

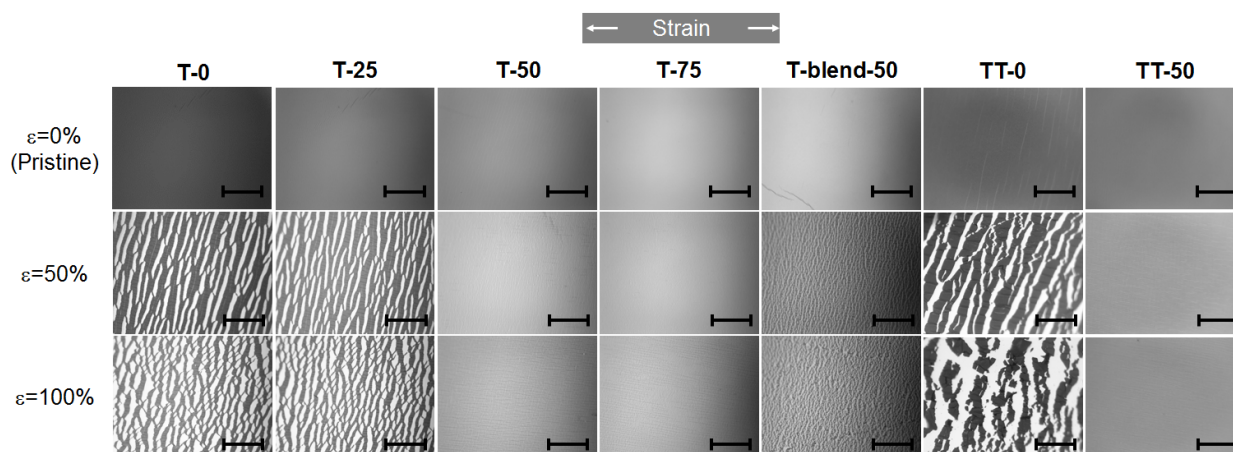


Figure S5. Optical micrographs demonstrating the cracking behavior of BCP and blend thin films on PDMS at 0, 50, and 100% strain, 100 cycles, scale bar, 500 μm .

Organic Field-effect Transistor (OFET) Measurement

Highly doped n-type Si wafers ($0.001\text{--}0.005\ \Omega\ \text{cm}$) with 300 nm of thermal oxide were sonicated for 10 min each in detergent solution (2% Alconox in deionized (DI) water), DI water only, and isopropyl alcohol (IPA). The substrates were then treated with plasma (30 W) for 5 min at a base pressure of 200 mTorr, then placed in a 0.33 vol.% solution of octadecyltrichlorosilane (OTS) in cyclohexane for 18 min. Samples were rinsed with cyclohexane and then sonicated for 10 min in chloroform (CHCl_3) before spinning a 10 mg/mL solution of **PDPP-*b*-PCL** in CHCl_3 at 1500 rpm for 30 seconds. Samples were annealed at 100 °C for 1 h. 40 nm thick Au electrodes were then thermally evaporated with a length of 1000 μm and width of 30 μm . Samples were tested on a Keithley 4200, with transfer curves taken with a source-drain voltage of -50 V (in the saturation regime).

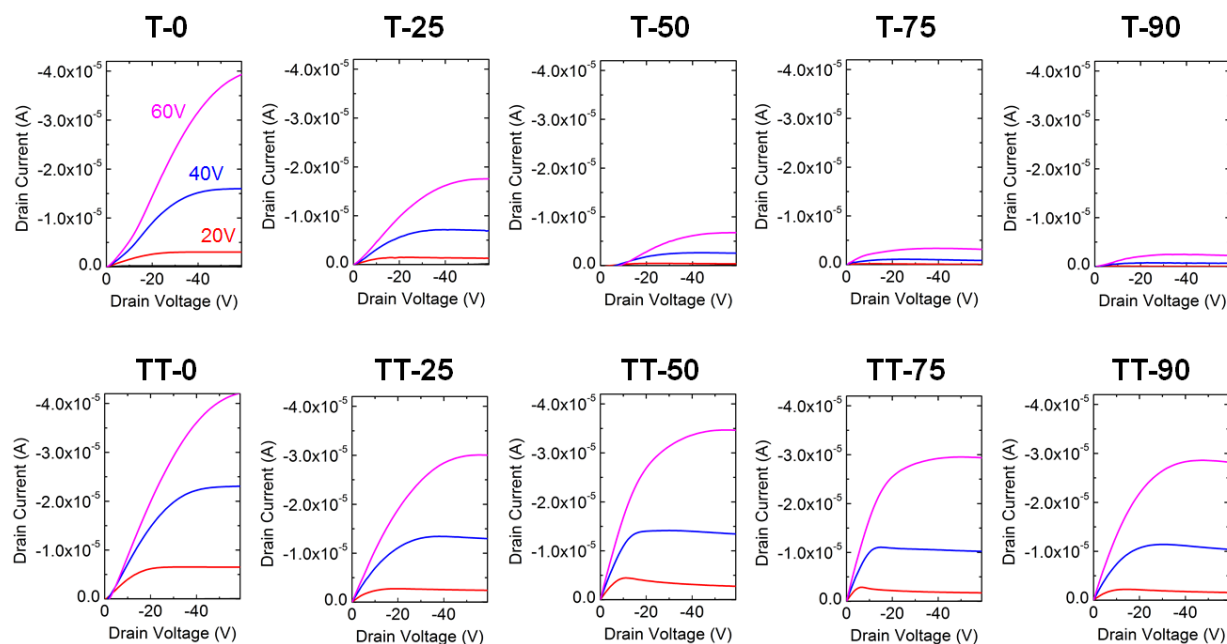


Figure S6. Output plots of BCPs as measured in OFETs.

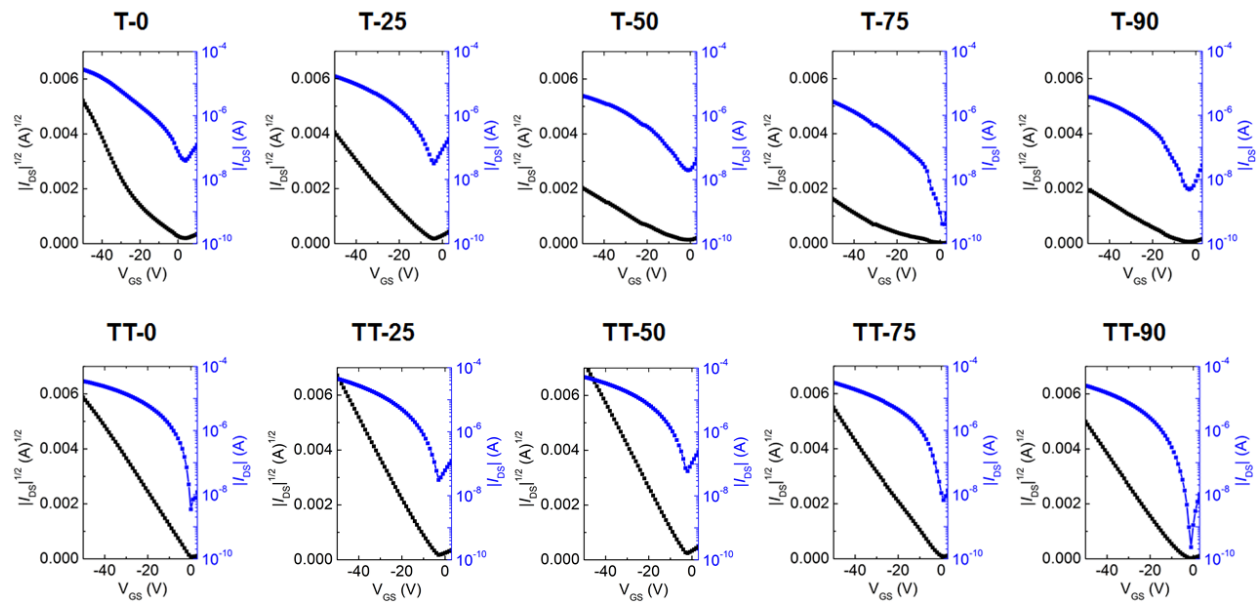


Figure S7. Transfer plots of **BCPs** as measured in OFETs.

Characterization of BCP Films Degradability

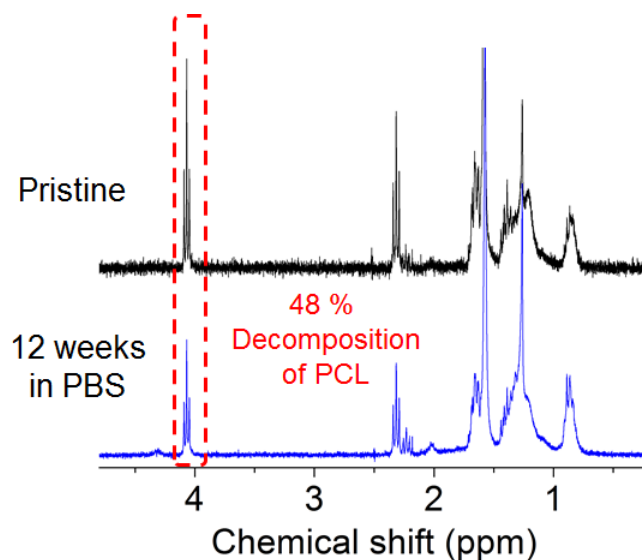


Figure S8. NMR spectra of **T-50** in CDCl_3 before (pristine) and after 12 weeks of exposing thin films to a in PBS at 37 °C.

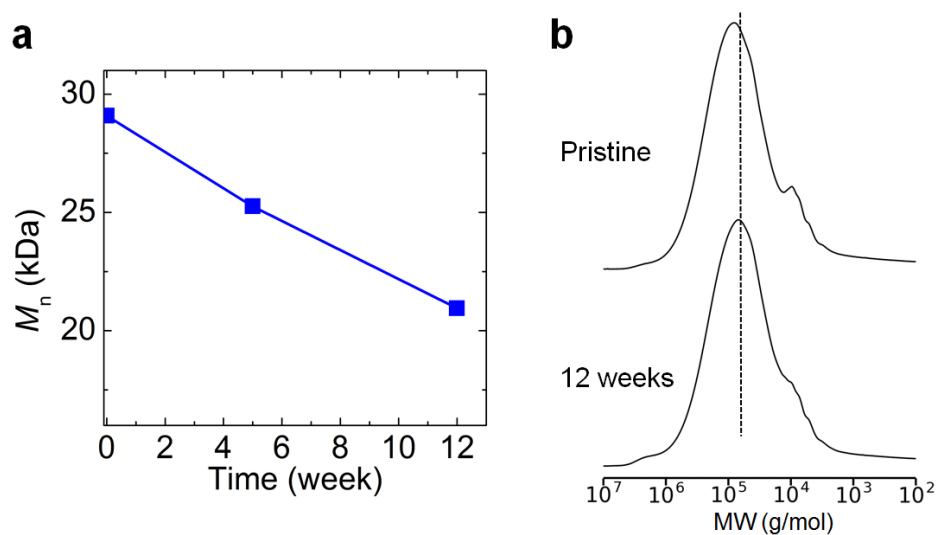


Figure S9. Characterization of BCP-films degradability. In vitro degradation of a **T-50** thin film for different immersion times in PBS at 37 °C. (a) Plot of the number average molecular weight (M_n) over time. (b) GPC traces before and after 12 weeks of immersion in PBS (Refractive Index Detector).

Base Etching of PCL to Examine Morphology of PDPP Segments

Using atomic force microscopy (AFM), we observed the micro-phase separation behavior of BCPs after exposure to an alkaline solution that etches the PCL to access the interconnectivity of the PDPP segments. The spin-coated BCP films on glass substrates were submerged in 0.5 M sodium hydroxide solution in water/methanol = 60/40 (volume/volume)% at 25 °C for 3 days and then washed with DI water. The based etching of PCL was monitored by ^1H NMR spectroscopy.

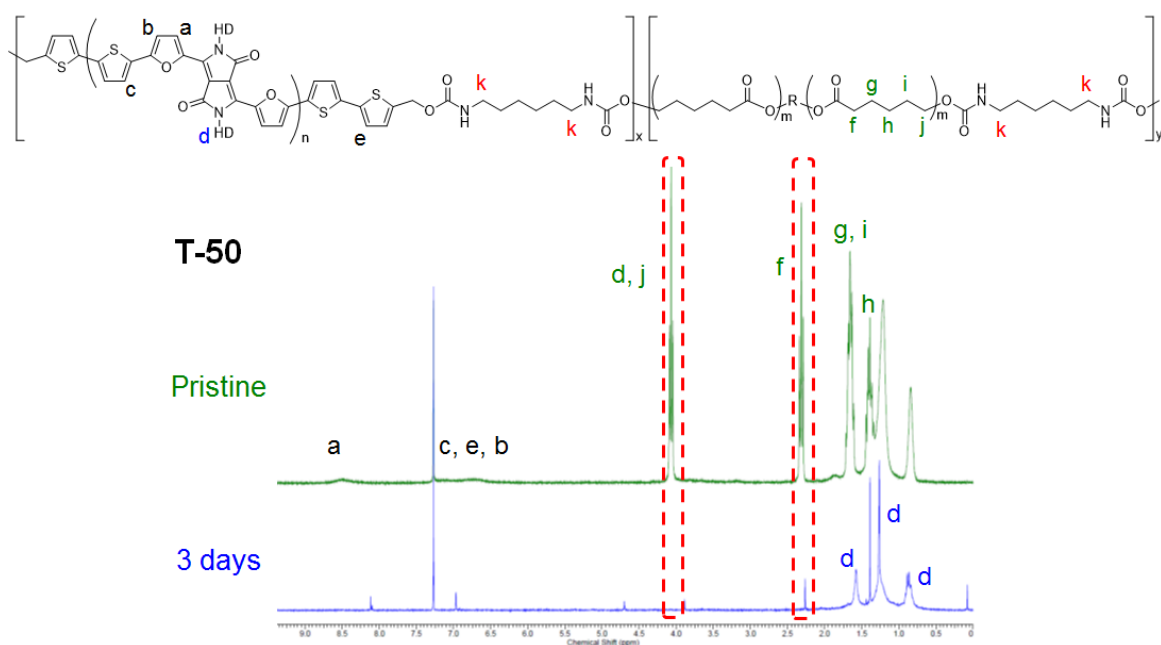


Figure S10. NMR spectra of **T-50** in CDCl_3 before (pristine) and after 3 days of exposing thin films to a basic solution (0.5 M sodium hydroxide solution in water/methanol = 60/40 (volume/volume)%).

General

Materials. All reagents were obtained from commercial suppliers and used without purification except for **DPP-Br**, which we synthesized according to previously established procedures.¹

NMR. All compounds were characterized by ¹H NMR (300 MHz, Bruker) using deuterated chloroform (CDCl₃) as a solvent. The residual chloroform peak at 7.28 ppm was used to calibrate the chemical shifts for ¹H NMR.

Gel Permeation Chromatography (GPC). GPC was performed in CHCl₃ using an Agilent 1260 Separation Module equipped with a 1260 Refractive Index Detector and a 1260 Photodiode Array Detector. Molecular weights were calculated relative to linear polystyrene (PS) standards.

Preparation of Substrates for Mechanical Testing. Glass slides, cut into squares (1 in × 1 in) with a diamond-tipped scribe, were used as substrates for the polymer thin films. The slides were thoroughly cleaned in an ultrasonic bath in the following sequence of 10 min steps: powdered Alconox detergent dissolved in DI water, DI water only, acetone, and then IPA. After that, the slides were dried with compressed (house) air and then treated with plasma (30 W) for 5 min at a base pressure of 200 mTorr of air to remove residual organic debris and improve surface wettability.

Preparation of Films. Solutions of BCPs in CHCl₃ (10 mg mL⁻¹) were prepared and allowed to stir overnight. Prior to use, all solutions were slightly heated (~15 s) with a heat gun to promote dissolution of the polymer; the solutions were then filtered with 0.45 μm PTFE filters, immediately after which they were spin-coated (Headway Research PWM32) onto the cleaned glass substrates at 1000 rpm (ramping at 500 rpm s⁻¹) for 120 s. These conditions produced films of thicknesses ranging from 100 to 150 nm as determined by profilometry (Dektak 150 Surface Profiler).

Ultraviolet-Visible (UV-vis) Spectroscopy. Once the freshly prepared thin films had dried under dynamic vacuum for 15 min, their as-cast UV-vis spectra were acquired using an Agilent 8453 UV-vis spectrometer. The range of wavelengths measured was from 300 to 1100 nm with a sampling increment of 1 nm.

Synthesis

All reactions were carried out under nitrogen with standard Schlenk techniques.

T-0: **DPP-Br** (499 mg, 0.570 mmol), 2,5-bis(trimethylstannyl)-thiophene (**T**) (247 mg, 0.600 mmol), 5-bromo-2-thiophenemethanol (**T-OH**) (11.9 mg, 0.060 mmol), tris(dibenzylideneacetone)dipalladium(0) ($\text{Pd}_2(\text{dba})_3$, 2.7 mol %), and tri(o-tolyl)phosphine ($\text{P}(\text{o-tol})_3$, 10.7 mol %) were charged within a 25 mL 3-necked flask, cycled with nitrogen, and subsequently dissolved in 10 mL of degassed chlorobenzene (CB). The mixture was stirred for 20 h at 110 °C. The reaction mixture was allowed to cool to 25 °C, 5 mL of CHCl_3 were added, and the polymer precipitated into methanol (200 mL). The precipitate was purified via Soxhlet extraction for 4 h with methanol and 6 h with acetone, followed by collection in CHCl_3 . The polymer **T-0** was obtained as a dark blue solid (428 mg). GPC analysis: see **Table S1**.

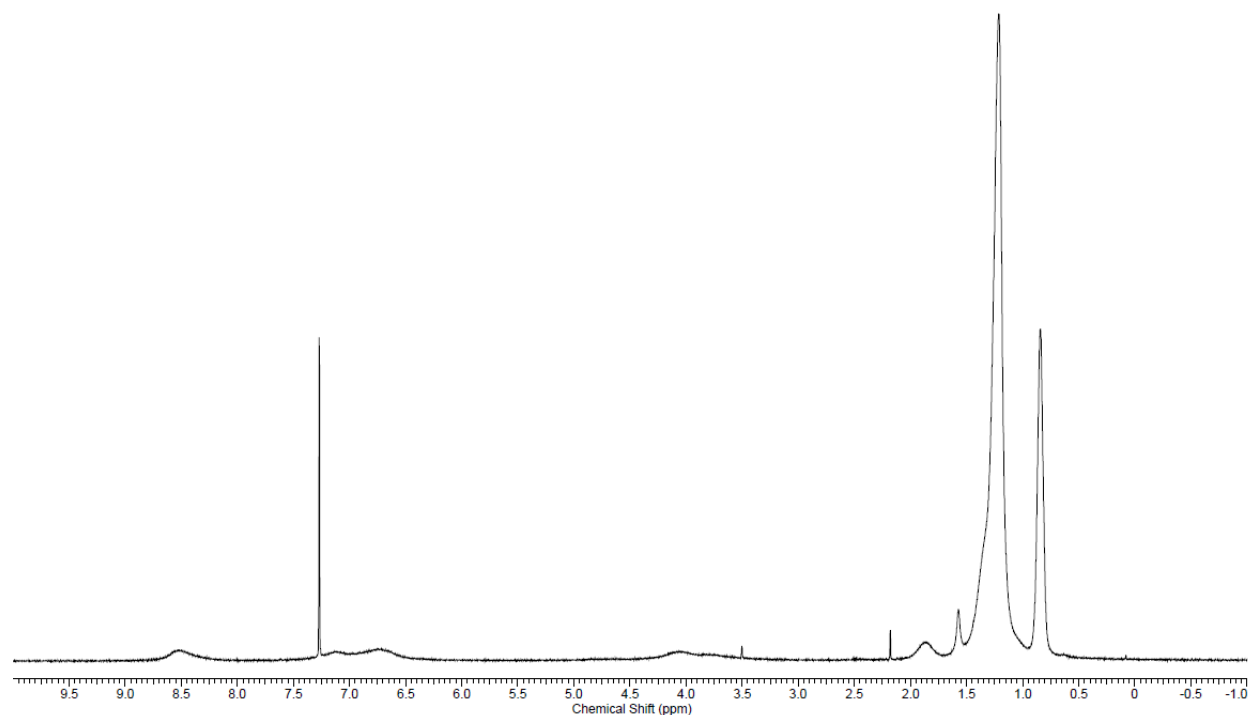


Figure S11. ^1H NMR spectrum of the obtained **T-0** in CDCl_3 at 25 °C.

TT-0: DPP-Br (332 mg, 0.380 mmol), 2,5-Bis(trimethylstannyl)-thieno[3,2-*b*]thiophene (**TT**) (186 mg, 0.400 mmol), 5-bromo-2-thiophenemethanol (**T-OH**) (7.72 mg, 0.040 mmol), Pd₂(dba)₃ (2.7 mol %), and P(*o*-tol)₃ (10.7 mol %) were charged within a 25 mL 3-necked flask, cycled with nitrogen, and subsequently dissolved in 6.5 mL of degassed CB. The mixture was stirred for 20 h at 110 °C. The reaction mixture was allowed to cool to 25 °C, 5 mL of CHCl₃ were added, and the polymer precipitated into methanol (200 mL). The precipitate was purified via Soxhlet extraction for 2 h with methanol and 4 h with acetone, followed by collection in CHCl₃. The polymer **TT-0** was obtained as a dark blue solid (323 mg). GPC analysis: see **Table S1**.

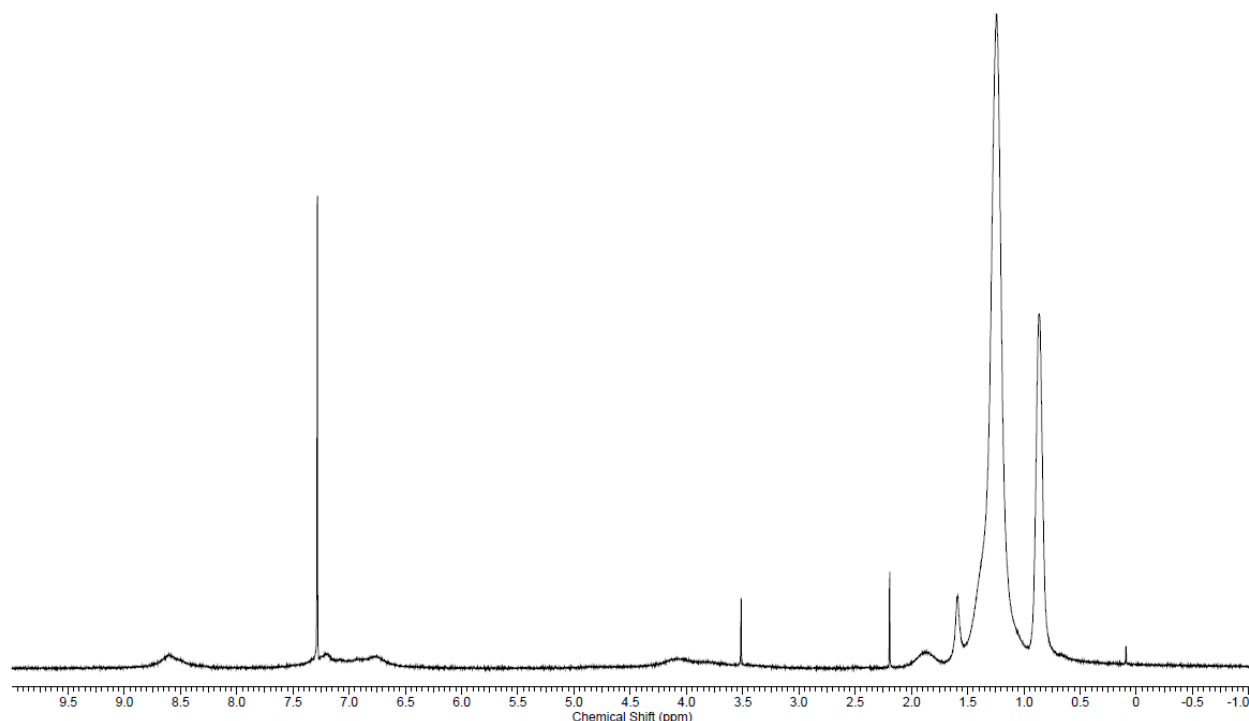


Figure S12. ¹H NMR spectrum of the obtained **TT-0** in CDCl₃ at 25 °C.

PCL: ϵ -Caprolactone (**ϵ -CL**) (2.28 g, 20.0 mmol) and 1,6-hexanediol (**HDO**) (11.8 mg, 0.10 mmol), were charged within a 25 mL round-bottom flask, cycled with nitrogen and subsequently dissolved in 5 mL of degassed dichloromethane (CH_2Cl_2). Then, a 1.0 wt% CH_2Cl_2 -containing solution of trifluoromethanesulfonimide (**HNTf₂**) (2.811mg, 0.010mmol) was added. The mixture was stirred for 68 h at 25 °C. After that, 5 mL of CHCl_3 were added to the reaction mixture, and the polymer precipitated into methanol (90 mL). The precipitate was collected via centrifugation. The polymer **PCL** was obtained as a white solid (428 mg). GPC analysis: see **Table S1**.

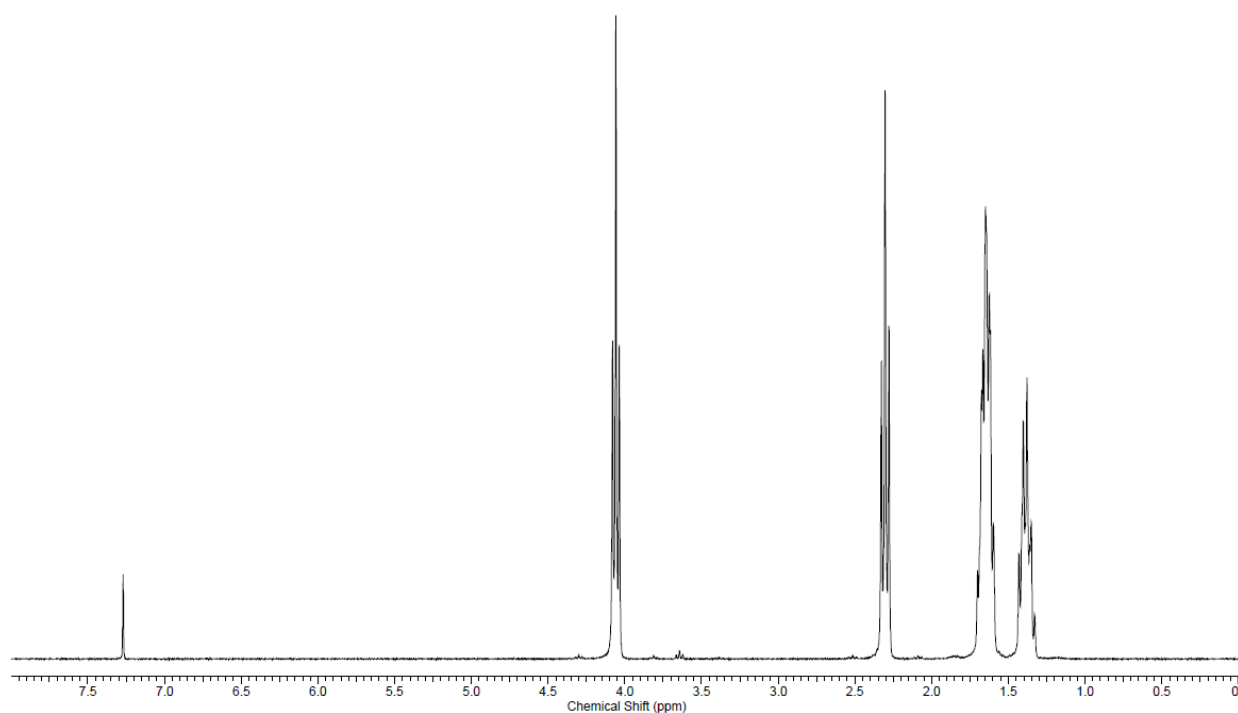


Figure S13. ^1H NMR spectrum of the obtained **PCL** in CDCl_3 at 25 °C.

T-50: **T-0** (75 mg, 3.7 mmol) and **PCL** (75 mg, 4.1 mmol) were charged within a 10 mL round-bottom flask, cycled with nitrogen, and subsequently dissolved in 1.5 mL of degassed CHCl_3 . Then, a 0.5 wt% CHCl_3 -containing solution of hexamethylene diisocyanate (**HMDI**) (1.30 mg, 7.8 mmol) was added. The mixture was stirred for 190 h at 50 °C. The polymer was precipitated into methanol (80 mL). The precipitate was collected via centrifugation. The polymer **T-50** was obtained as a dark blue solid (144 mg). GPC and NMR analysis: see **Table S1**.

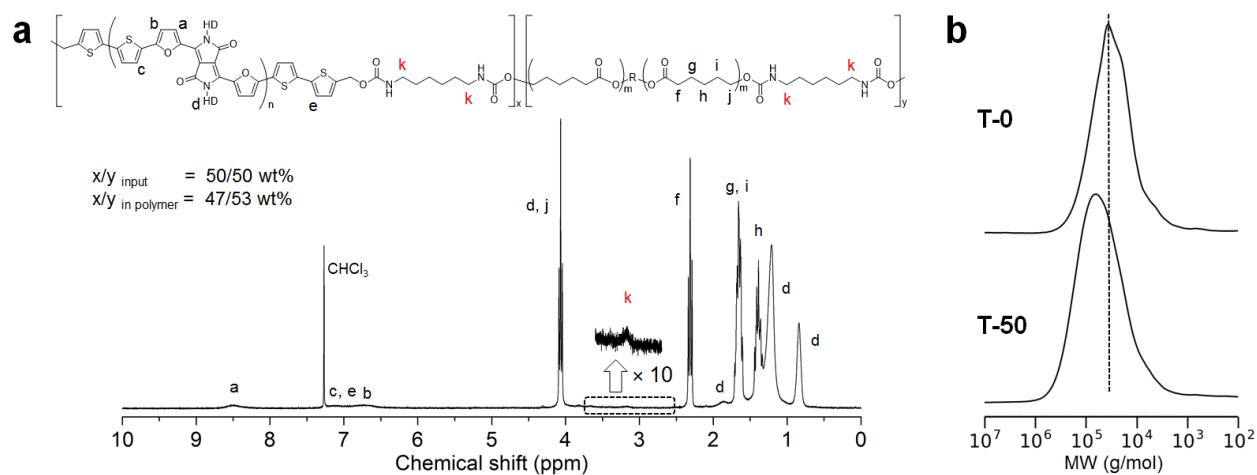


Figure S14. (a) ^1H NMR spectrum of the obtained **T-50** in CDCl_3 at 25 °C. (b) GPC traces of **T-0** and **T-50** (Refractive Index Detector).

The remaining BCPs were obtained by changing the weight fraction of **PCL** and/or using **TT-0**.

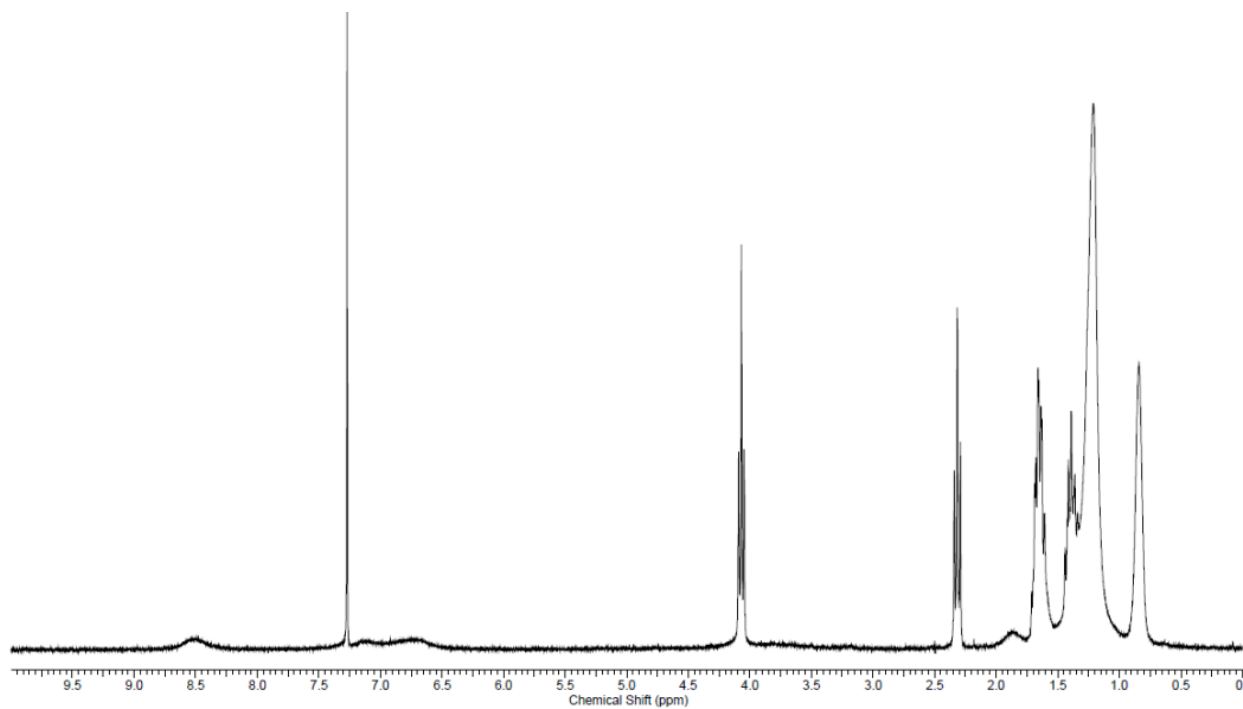


Figure S15. ^1H NMR spectrum of the obtained **T-25** in CDCl_3 at 25 °C.

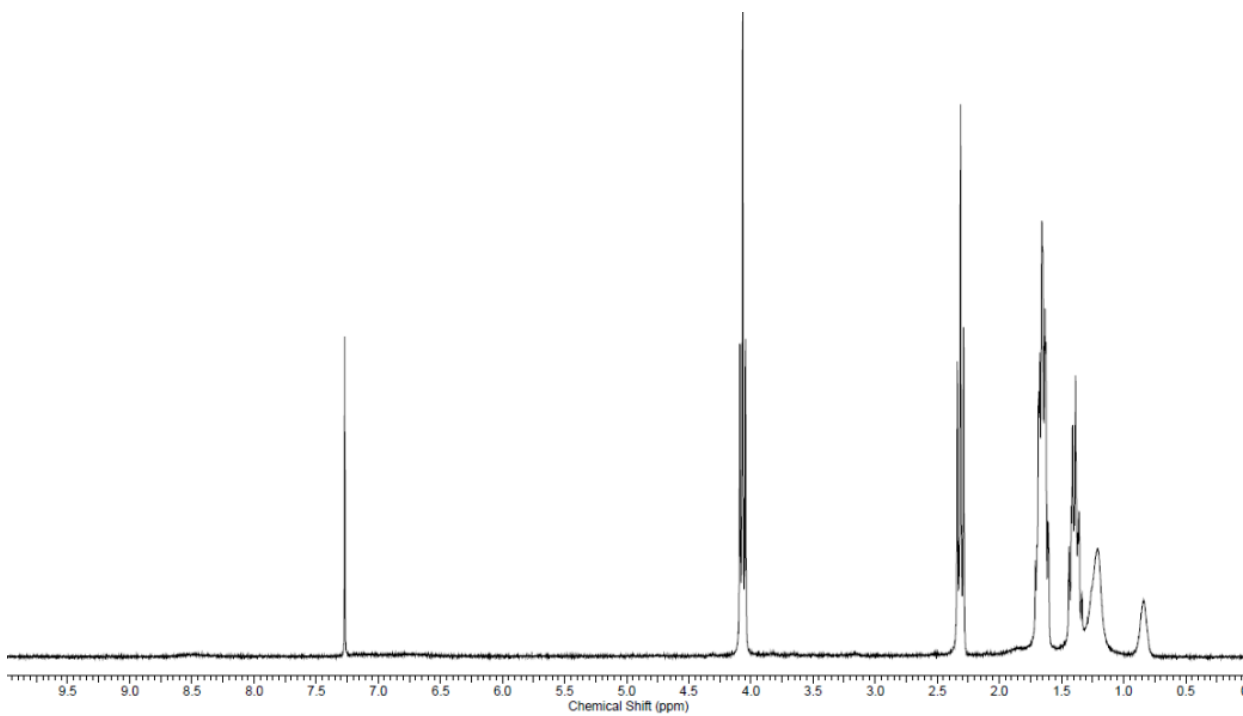


Figure S16. ^1H NMR spectrum of the obtained **T-75** in CDCl_3 at 25 °C.

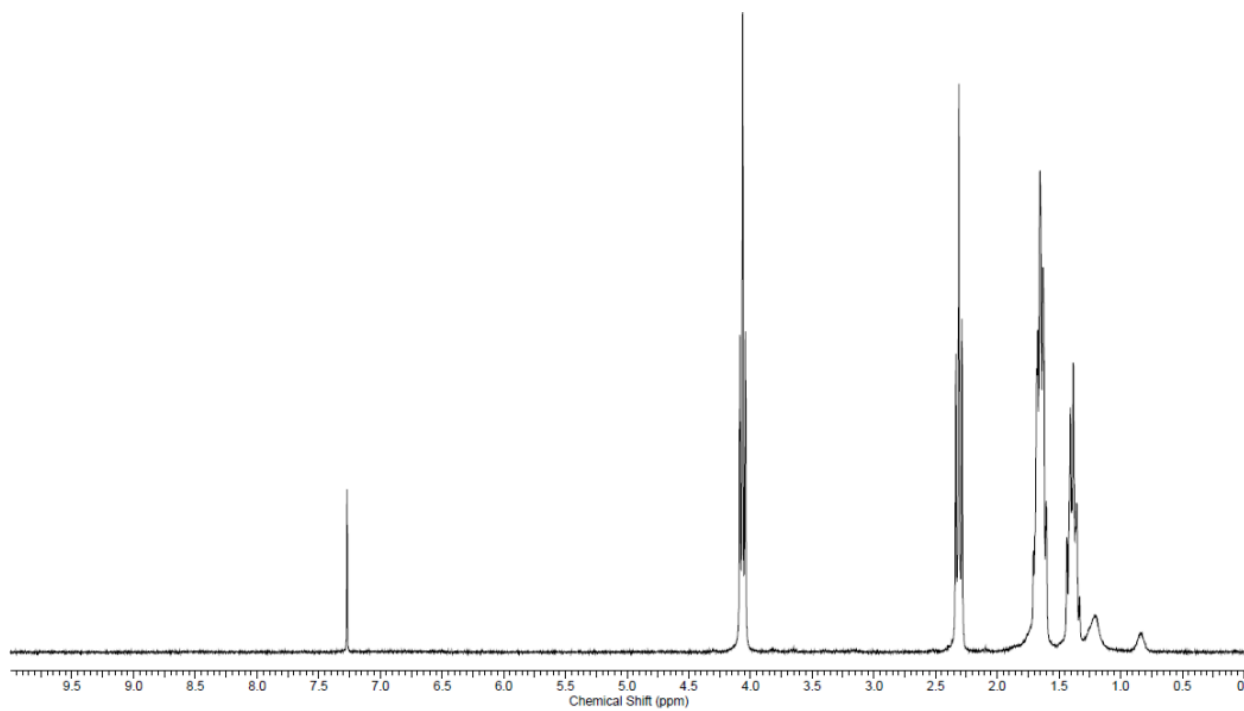


Figure S17. ^1H NMR spectrum of the obtained **T-90** in CDCl_3 at 25°C .

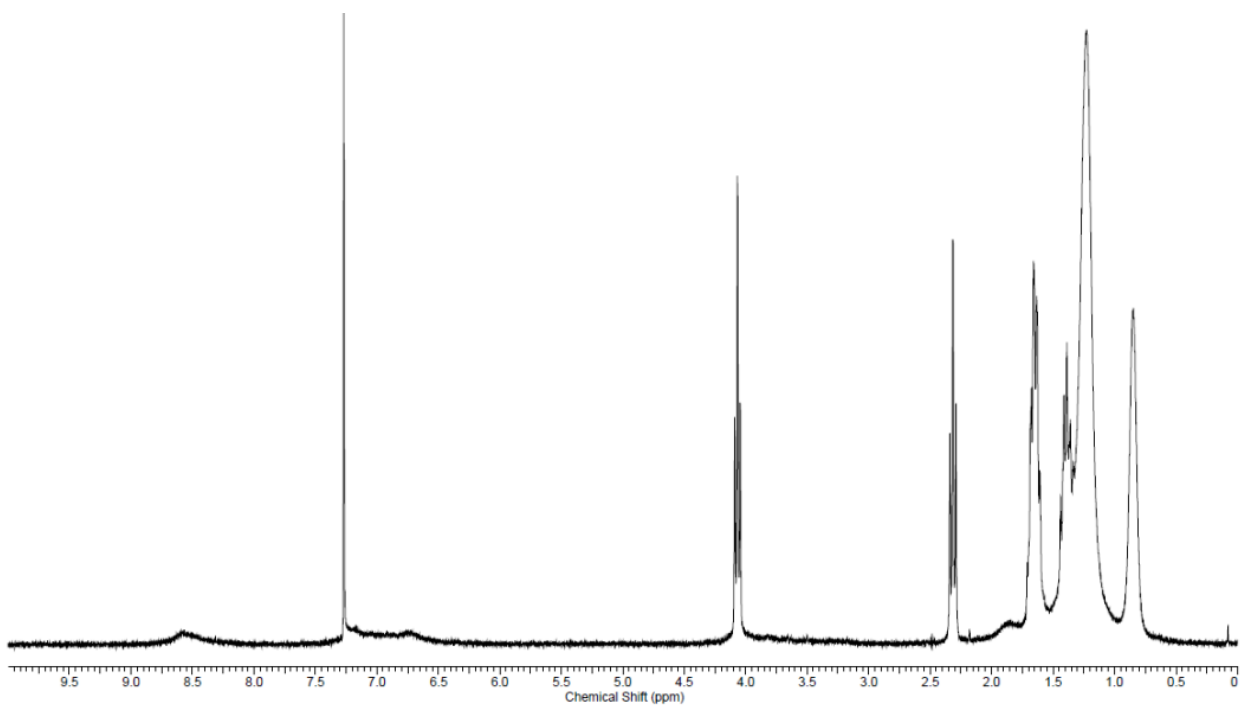


Figure S18. ^1H NMR spectrum of the obtained **TT-25** in CDCl_3 at 25°C .

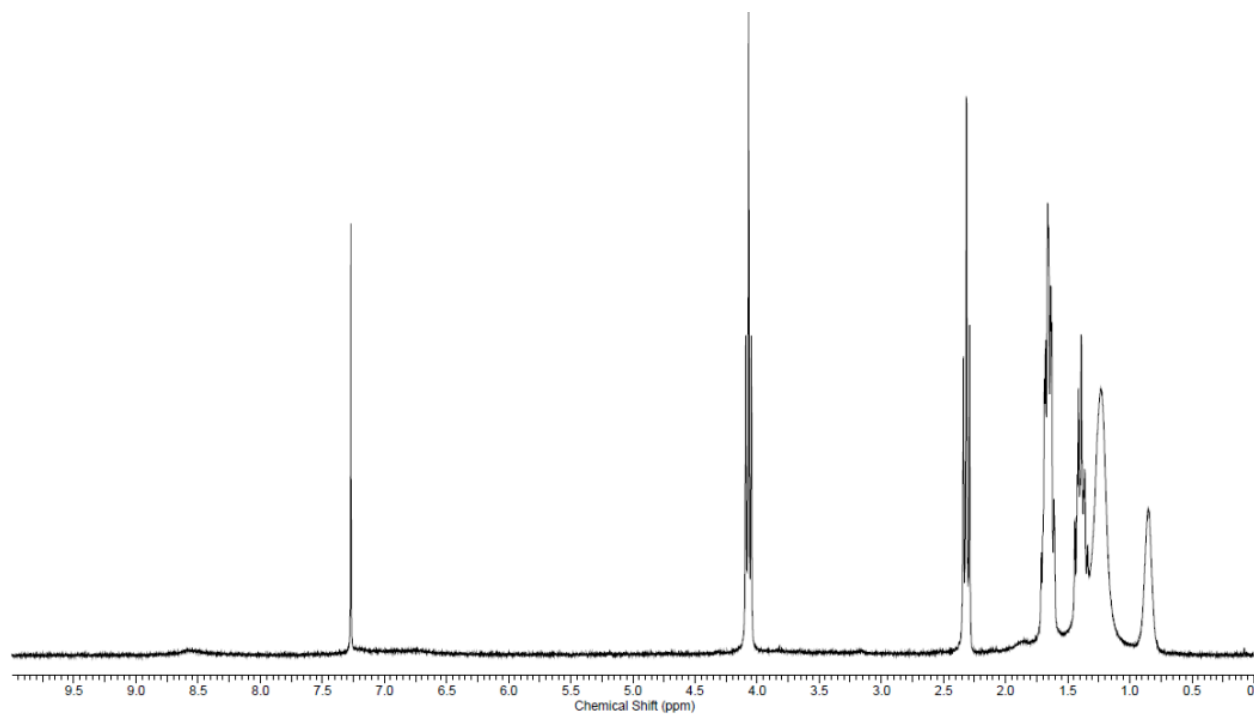


Figure S19. ^1H NMR spectrum of the obtained **TT-50** in CDCl_3 at 25 °C.

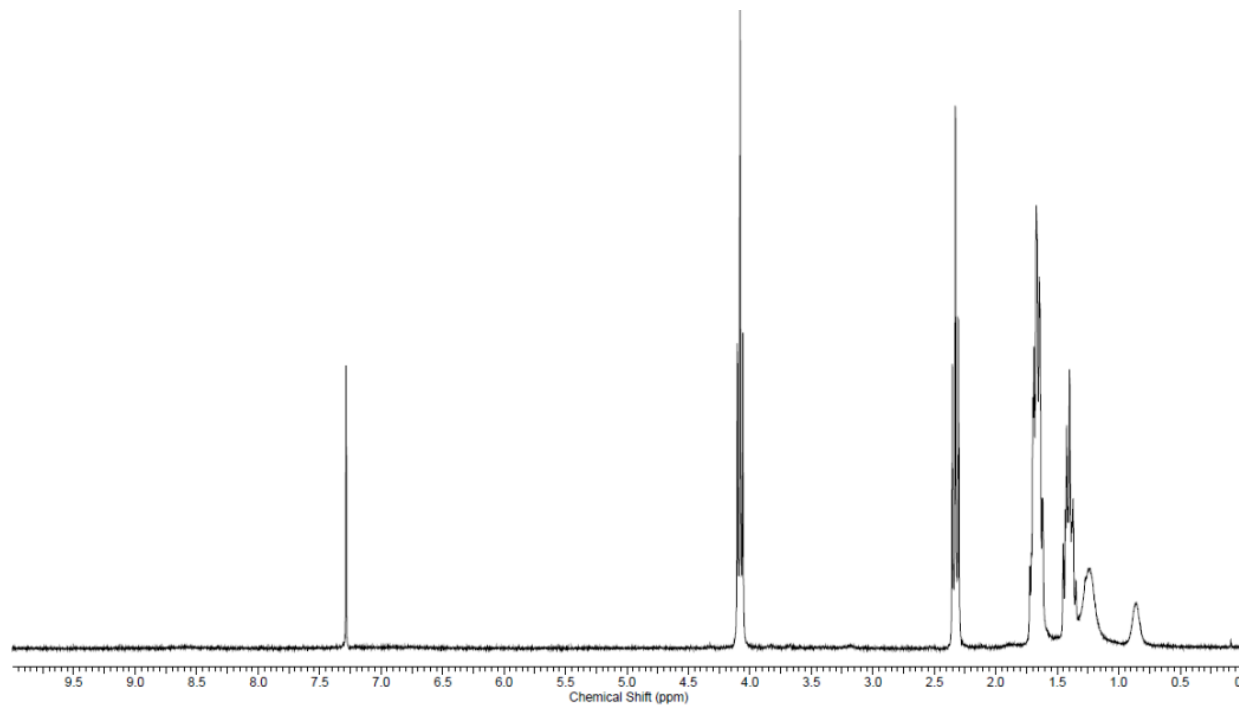


Figure S20. ^1H NMR spectrum of the obtained **TT-75** in CDCl_3 at 25 °C.

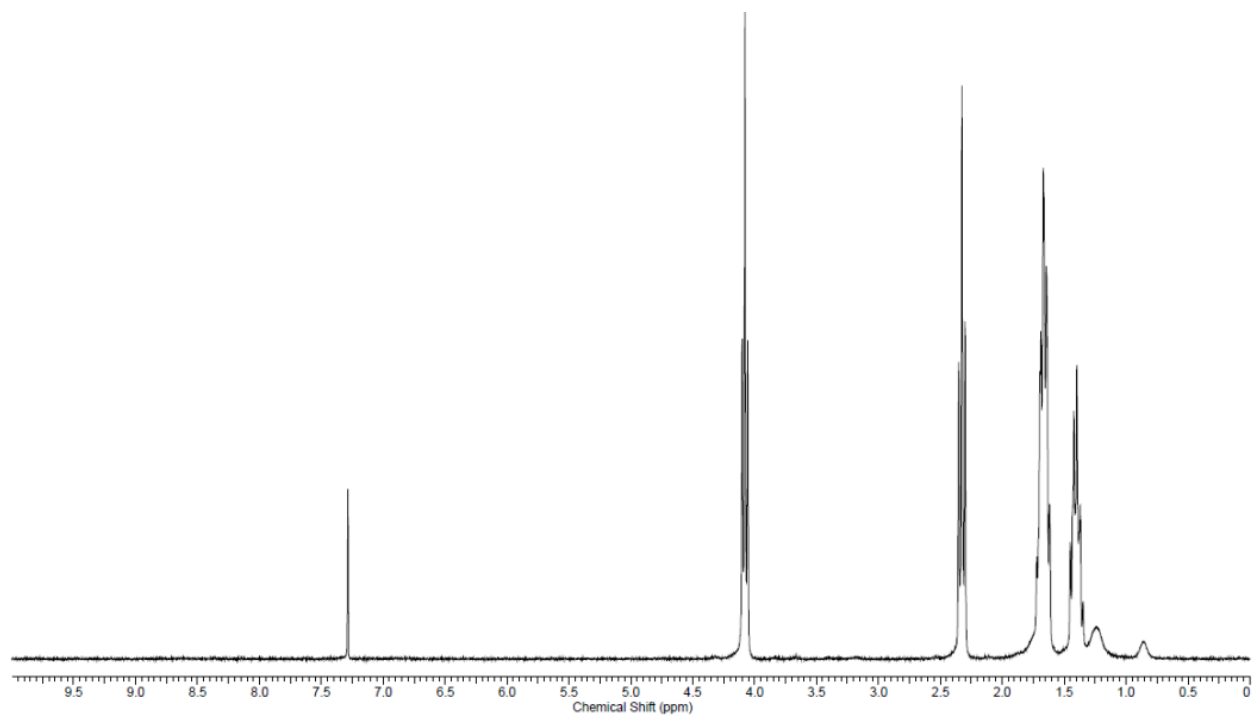


Figure S21. ^1H NMR spectrum of the obtained **TT-90** in CDCl_3 at 25°C .

Identification of Urethane Linkages by NMR

In order to assign the signal at 3.2 ppm—which appears during the formation of the block copolymer—to the methylene protons **k** (**Figure S14**), we reacted HMDI with MeOH to form the methyl carbamate product. The reaction is quantitative and forms a white powder which is fully soluble in methanol and chloroform. Its NMR is shown below in **Figure S22**. The signal at 3.18 ppm can be attributed to the methylene unit **c** and confirms the assignment of **k** at 3.2 ppm. The efficiency of the coupling reaction between PCL and PDPP could not be determined quantitatively by ^1H NMR due to the overlapping of the end-group signals with other polymeric protons. However, the NMRs of BCP do not show a singlet at 3.67 ppm (signal **a**) which would originate from the reaction of the unreacted isocyanate end-group with methanol upon work-up. The absence of signal at 3.67 ppm, the presence of a broad signal at 3.2 ppm and the GPC traces indicate that we are, at least, forming diblock copolymers along with, statistically speaking, some smaller fraction of lower-order multiblock copolymers.

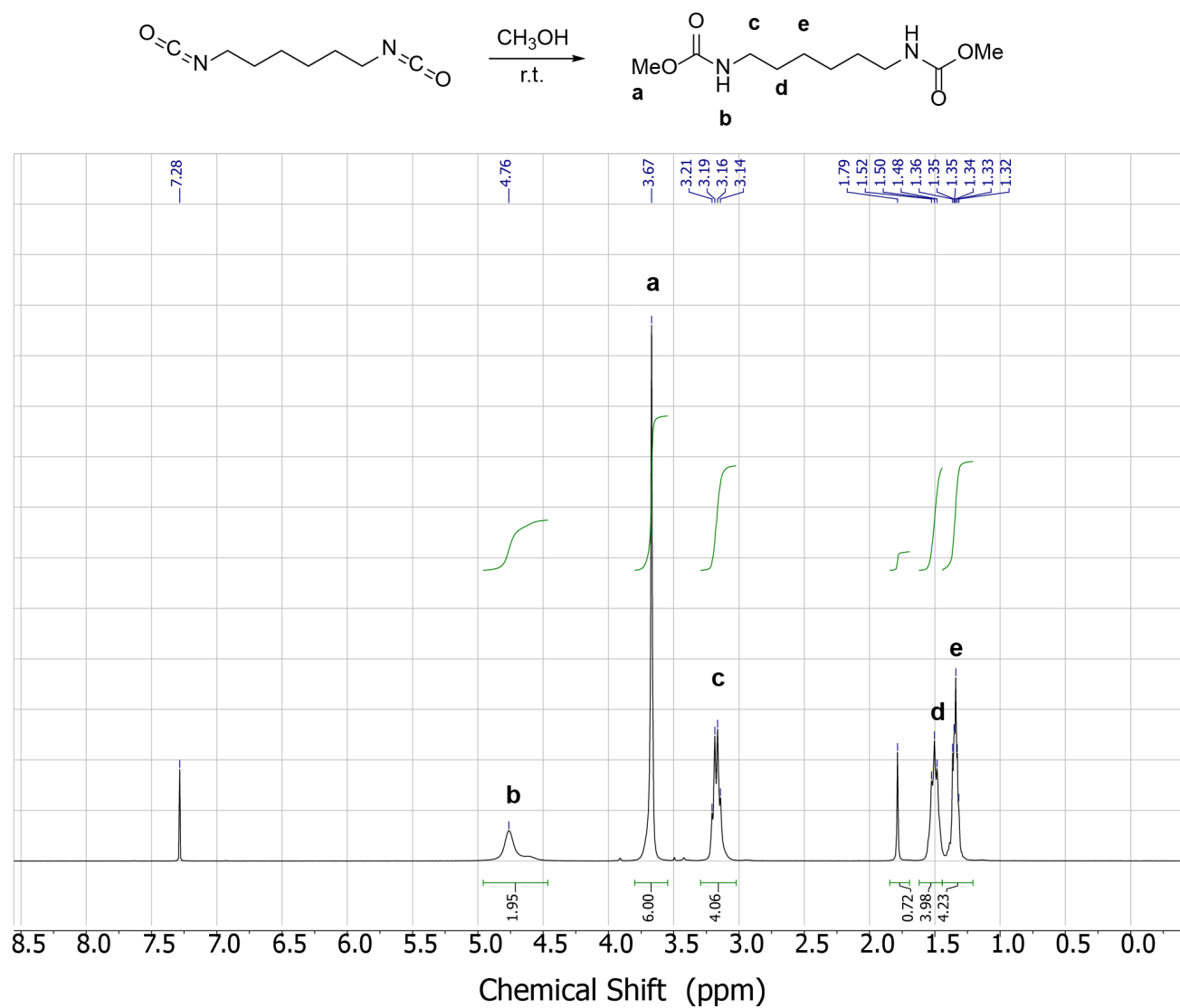


Figure S22. Reaction of HMDI with methanol and ¹H NMR spectrum of the obtained product.

GPC Characterization

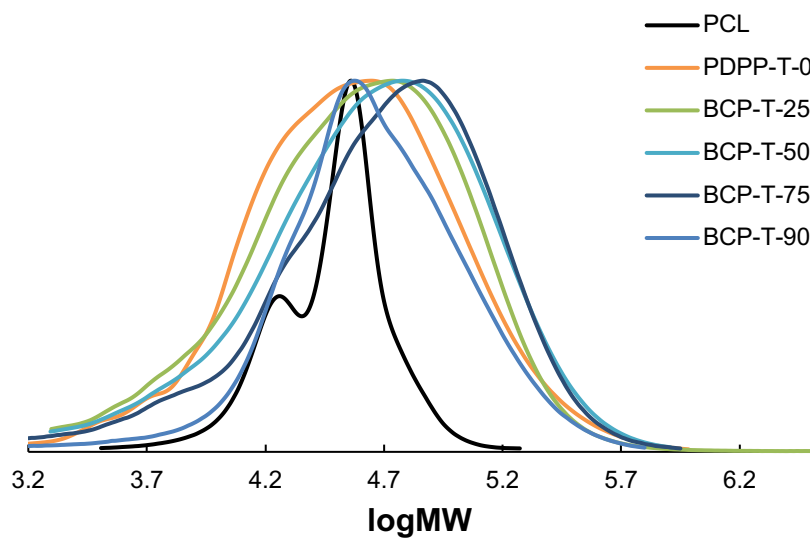


Figure S23. Normalized GPC traces from refractive index detector of PCL, PDPP-T-0 and BCP-T-25 to T-90.

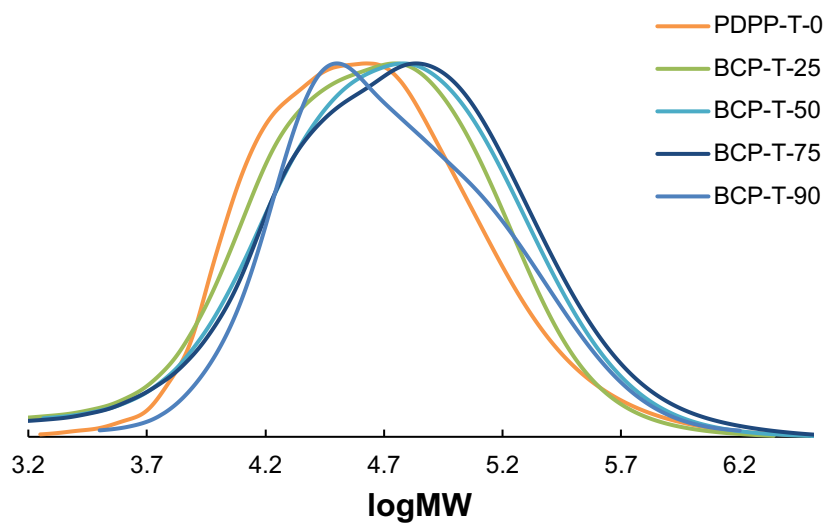


Figure S24. Normalized GPC traces from UV-Vis detector at 800 nm of PDPP-T-0 and BCP-T-25 to T-90. (PCL is not UV-Vis active and therefore could not be detected).

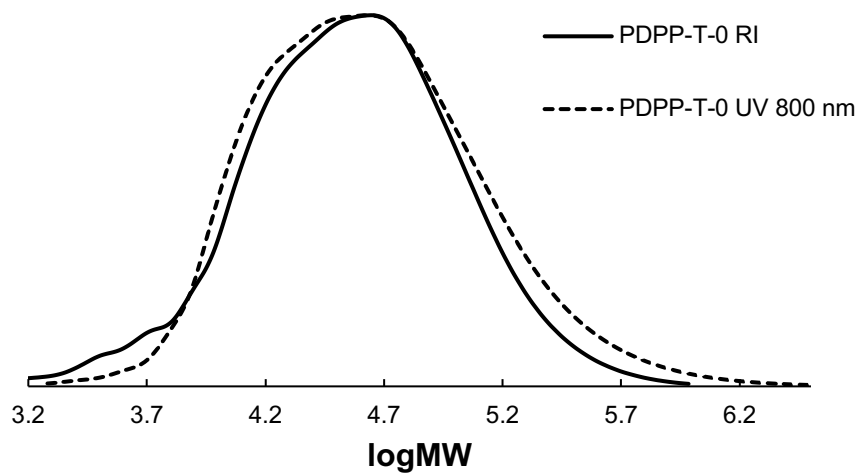


Figure S25. Normalized GPC traces from RI and UV-Vis detector at 800 nm of PDPP-T-0.

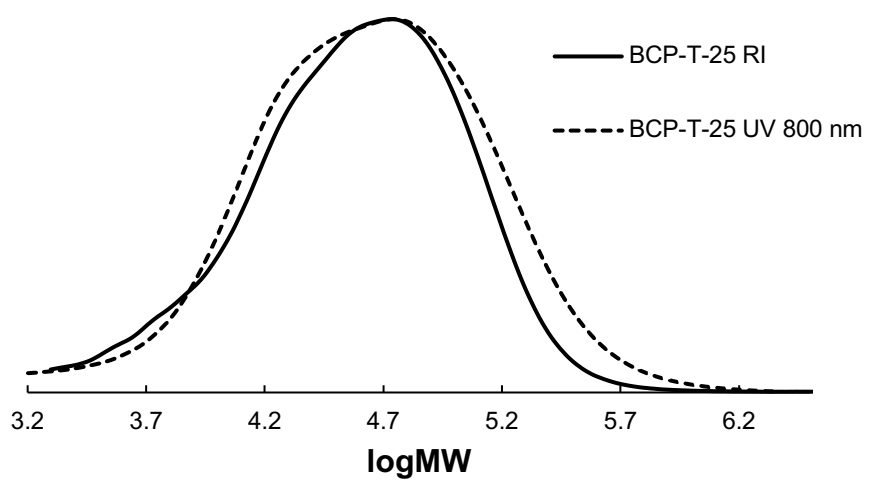


Figure S26. Normalized GPC traces from RI and UV-Vis detector at 800 nm of PDPP-T-25.

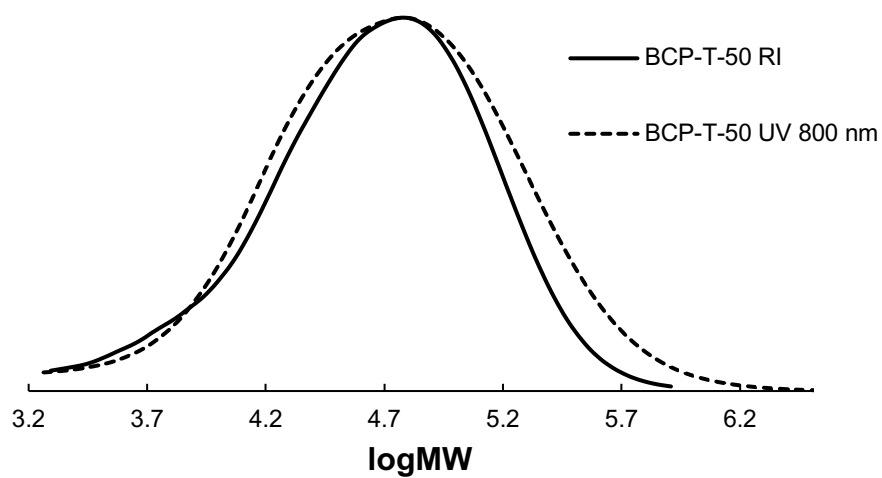


Figure S27. Normalized GPC traces from RI and UV-Vis detector at 800 nm of PDPP-T-50.

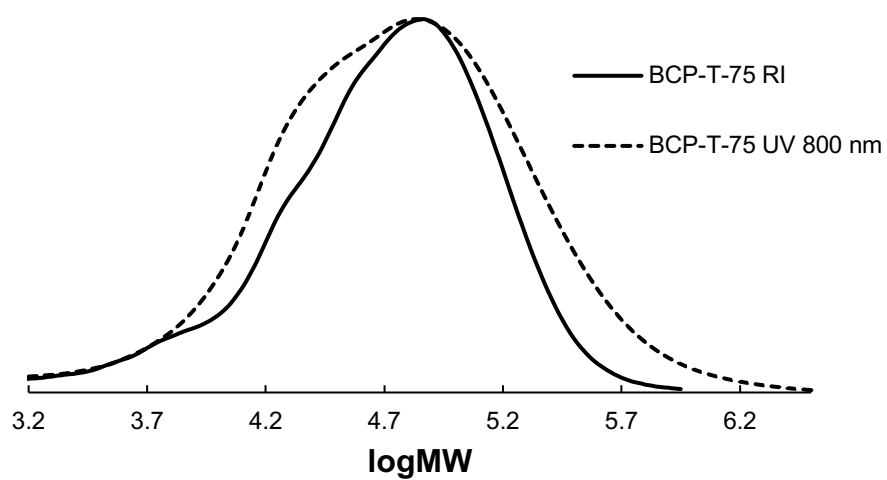


Figure S28. Normalized GPC traces from RI and UV-Vis detector at 800 nm of PDPP-T-75.

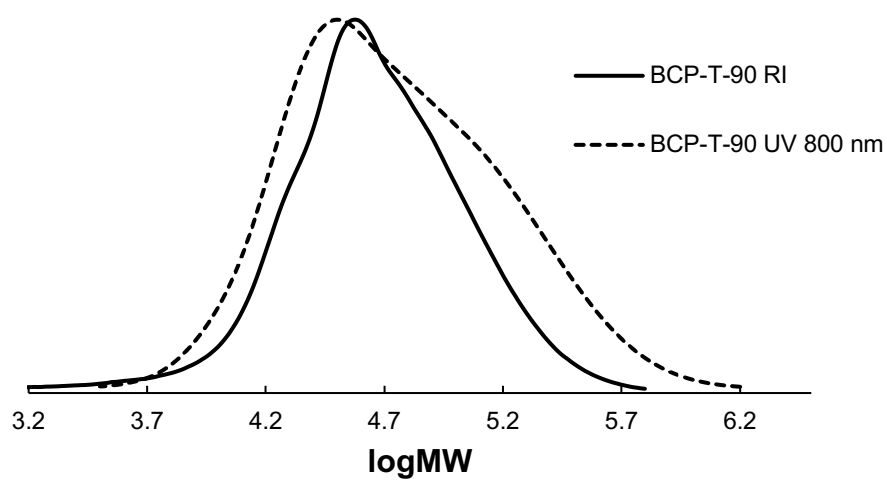


Figure S29. Normalized GPC traces from RI and UV-Vis detector at 800 nm of PDPP-T-90.

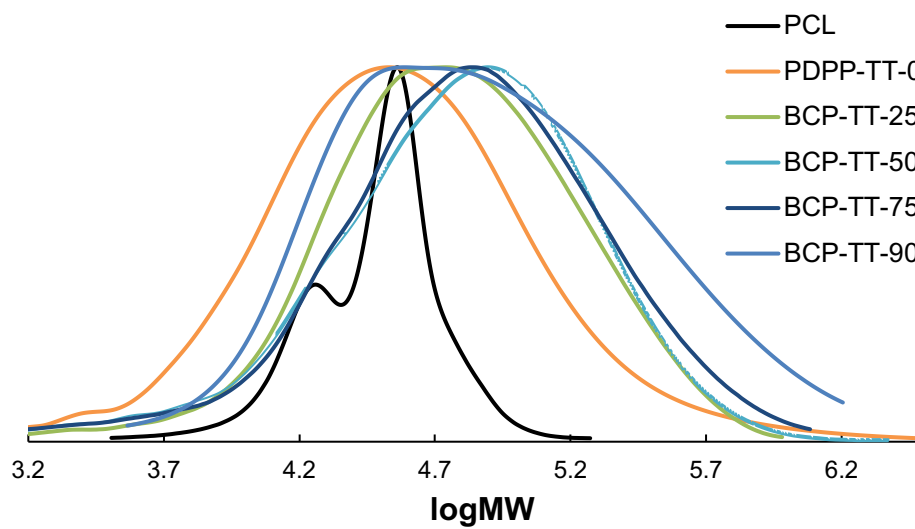


Figure S30. Normalized GPC traces from refractive index detector of PCL, PDPP-TT-0 and BCP-TT-25 to TT-90.

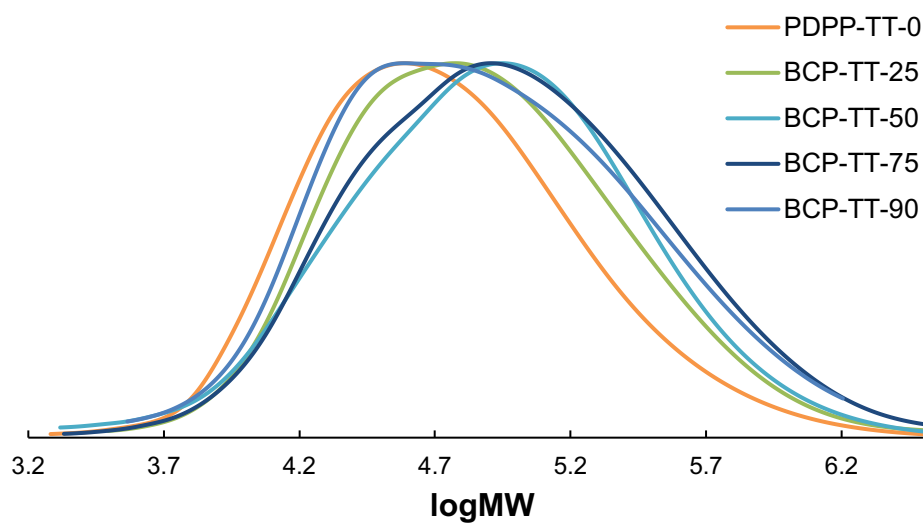


Figure S31. Normalized GPC traces from UV-Vis detector at 800 nm of PCL, PDPP-TT-0 and BCP-TT-25 to TT-90.

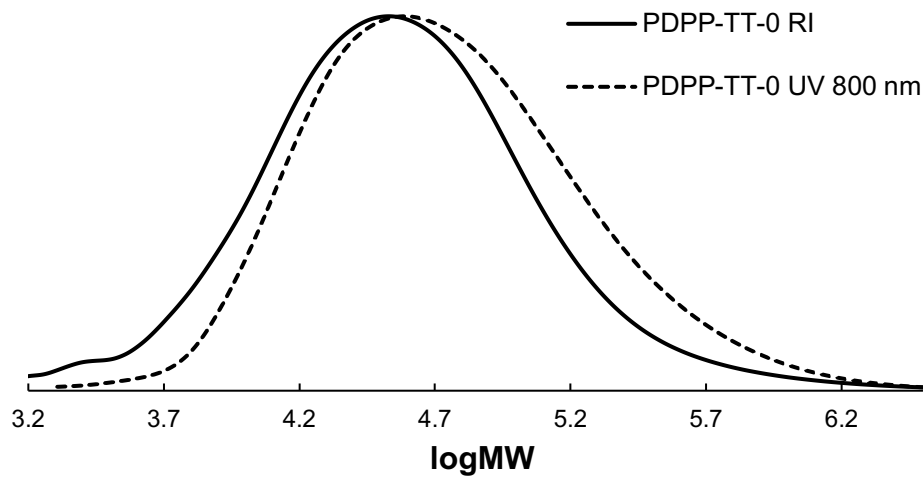


Figure S32. Normalized GPC traces from RI and UV-Vis detector at 800 nm of PDPP-TT-0.

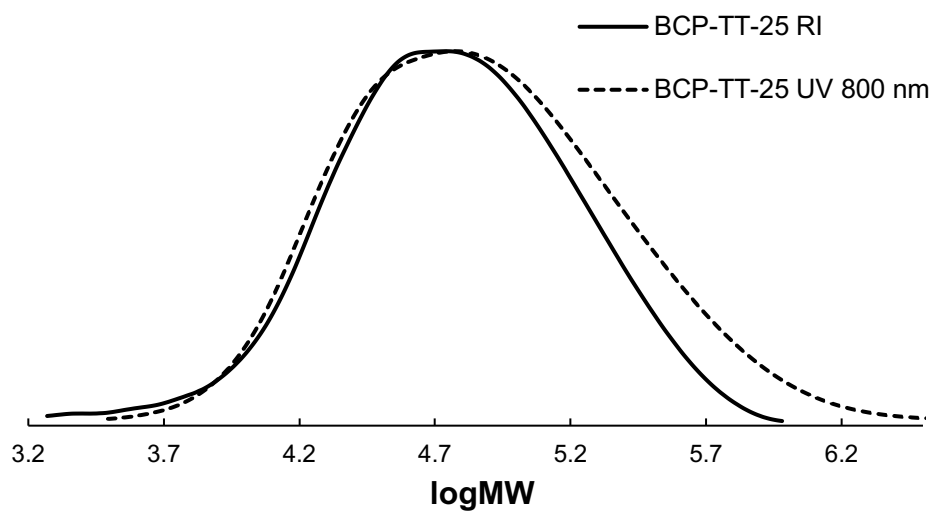


Figure S33. Normalized GPC traces from RI and UV-Vis detector at 800 nm of PDPP-TT-25.

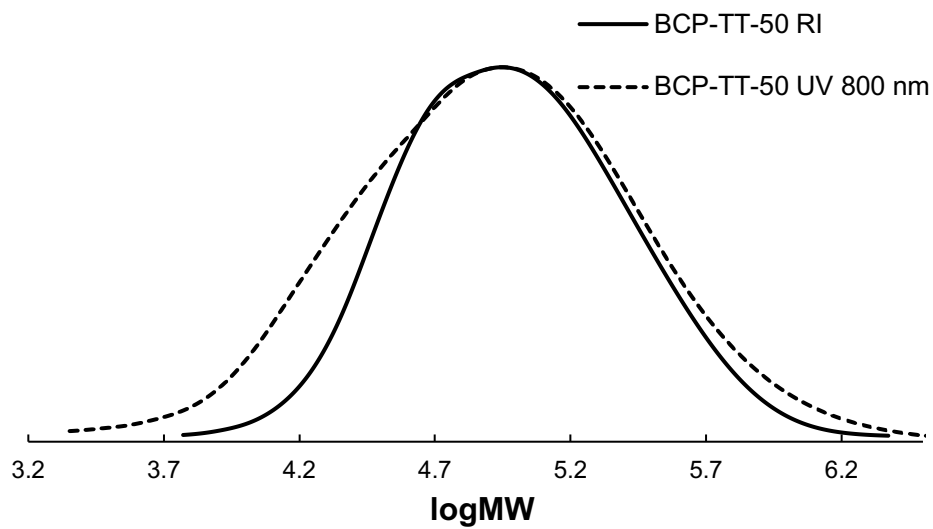


Figure S34. Normalized GPC traces from RI and UV-Vis detector at 800 nm of PDPP-TT-50.

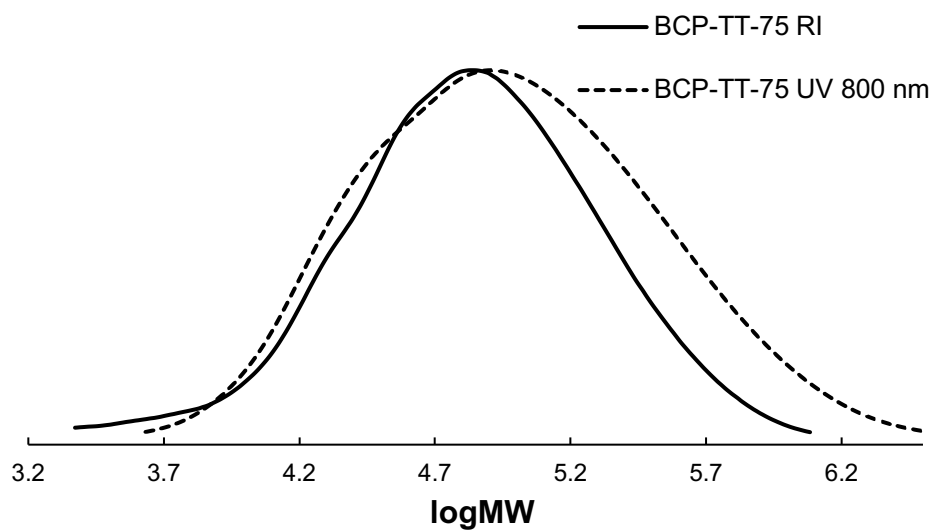


Figure S35. Normalized GPC traces from RI and UV-Vis detector at 800 nm of PDPP-TT-75.

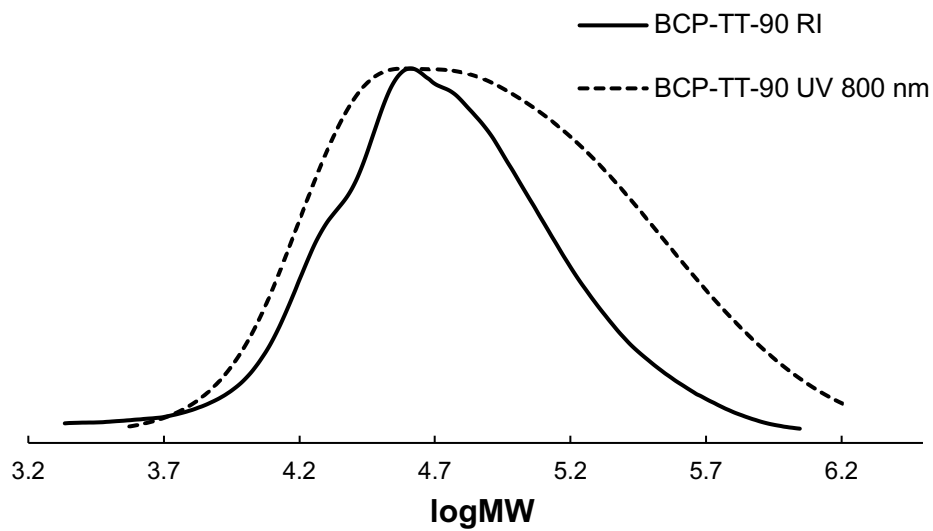


Figure S36. Normalized GPC traces from RI and UV-Vis detector at 800 nm of PDPP-TT-90.

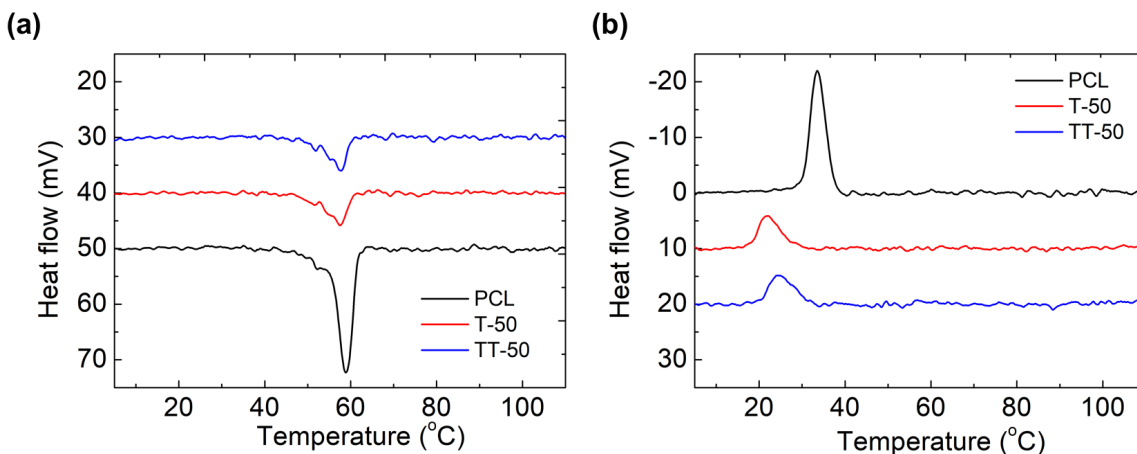


Figure S37. Heating (a) and cooling (b) DSC traces of 100% PCL blocks, 50% PCL/50% PDPP-T blocks, 50% PCL/50% PDPP-TT.

UV-Vis Characterization

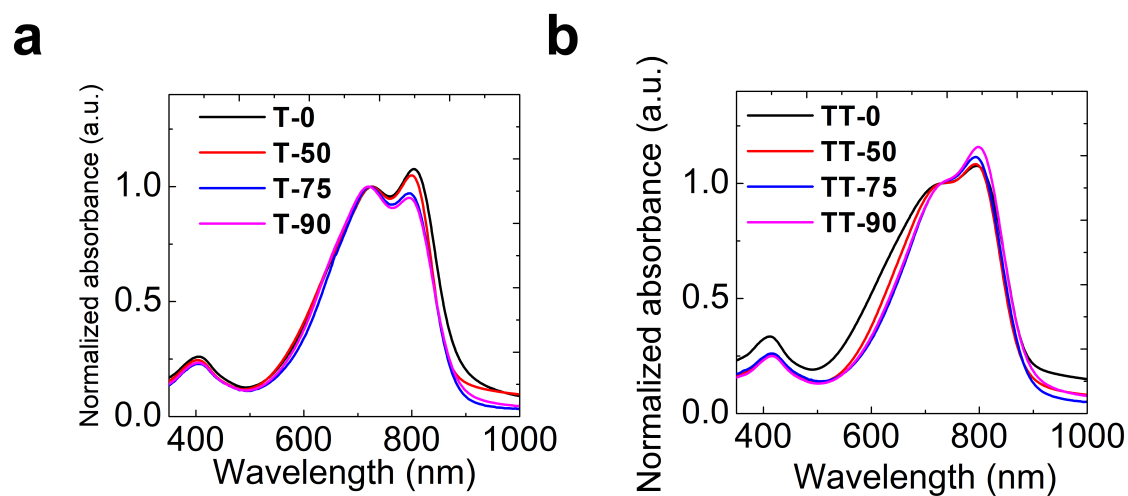


Figure S38. UV-vis spectra for the T series (a) and TT series (b) for 0%, 50%, 75%, and 90% PCL. Normalized to the $A_{0.1}$ peak (720 nm for the T-series, 739 nm for the TT-series).



Figure S39. T-0 (a) and T-75 (b) films strained to their respective failure points.

References

- (1) Yiu, A. T.; Beaujuge, P. M.; Lee, O. P.; Woo, C. H.; Toney, M. F.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2012**, *134* (4), 2180.