Electronic supplementary information

Rapid flash annealing of thermally reactive copolymers in a roll-to-roll process for polymer solar cells

Martin Helgesen, Jon Eggert Carlé, Birgitta Andreasen, Markus Hösel, Roar Søndergaard, Kion Norrman and Frederik C. Krebs*

DTU Energy Conversion, Technical University of Denmark, Frederiksborgvej 399, DK-4000 Roskilde, Denmark.

e-mail: frkr@dtu.dk

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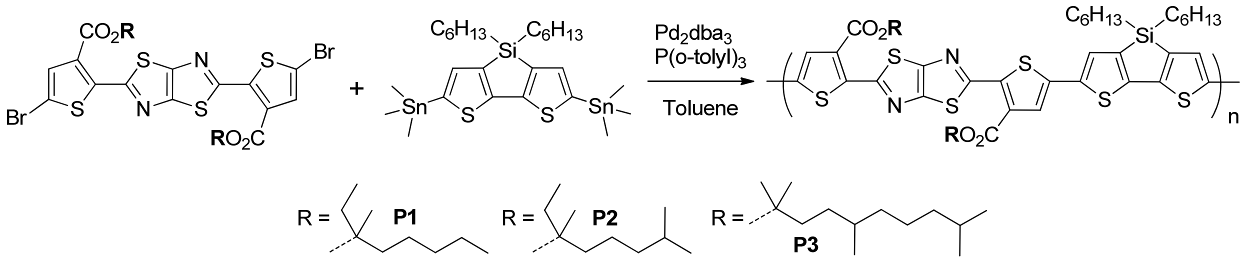
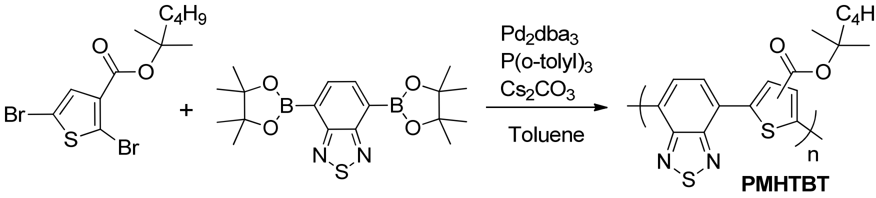
General experimental details

General methods, instrumentation and materials. Molecular weights were determined using size exclusion chromatography in HPLC-grade chloroform against polystyrene standards on a KNAUER chromatograph with a refractive index detector and a diode array UV-vis detector. UV-vis absorption spectra were measured with a Perkin-Elmer Lambda 900 spectrometer. FTIR spectroscopy was conducted with a Spectrum One from Perkin Elmer (4 cm^{-1} resolution, 32 scans summation). TGA experiments were performed with a dynamic heat rate (10 °C/min) under an nitrogen atmosphere (20 ml/min) in the temperature range 50-500 °C. Atomic Force Microscopy (AFM) imaging was performed on a N8 NEOS (Bruker Nano GmbH, Herzogenrath, Germany) operating in an intermittent contact mode using PPP-NCLR cantilevers (NANOSENSORS, Neuchatel, Switzerland). Images were recorded at a scan speed of 1 line s^{-1}. XPS analyses were performed on a KR (Thermo Electron Limited, Winsford, U.K.) using a monochromated Al KR X-ray source and a takeoff angle of 90° from the surface plane. Atomic concentrations were determined from surface spectra (0-1350 eV, 200 eV detector pass energy) and were calculated by determining the relevant integral peak intensities using a Shirley-type background. High-resolution C1s spectra were acquired with a detector pass energy of 25 eV. Unless stated otherwise all reagents and solvents were obtained from Aldrich and used without further purification. PCBM was purchased from Solenne BV with a purity of 99%. **P1-P3** and **PMHTBT** was prepared according to literature procedures[1,2] or slight modifications thereof.

Synthetic procedures and characterization data



General procedure for the Stille copolymerization. Bis(3-methyl-3-octanyl) 2,2'-(thiazolo[5,4-*d*]thiazole-2,5-diyl)bis(5-bromothiophene-3-carboxylate) (200 mg, 0.25 mmol), 4,4-dihexyl-2,6-bis(trimethylstannyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene (171 mg, 0.25 mmol), Pd_2dba_3 (11 mg, 0.012 mmol) and tri-(o-tolyl)phosphine (19 mg, 62 mmol) was mixed in dry degassed toluene (10 ml). The reaction mixture was heated to reflux for 48 hours under argon. After cooling to room temperature the mixture was poured into 100 ml methanol and the polymer was allowed to precipitate. The polymer was filtered and purified by Soxhlet extraction using methanol, hexane and chloroform. The chloroform phase was concentrated to a smaller volume in vacuum and precipitated in methanol (1:10). Filtration and drying in vacuum afforded **P1** as a dark blue solid. Yield: 237 mg (95 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.55 – 6.83 (br, 4H), 2.44 – 0.68 (br, 64H). SEC ($CHCl_3$): M_w = 32400, M_n = 9500, PDI = 3.4.



Poly[2,5-(2-methyl-2-hexyl-thiophene-3-carboxylate)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PMHTBT). 2-methyl-2-hexyl 2,5-dibromothiophene-3-carboxylate (457 mg, 1.19 mmol), 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*c*][1,2,5]thiadiazole (462 mg, 1.19 mmol), Pd_2dba_3 (55 mg, 60 μmol) and tri-(o-tolyl)phosphine (109 mg, 0.36 mmol) was dissolved in dry degassed toluene (10 ml) and stirred for 15 min at room temperature under argon. Then Cs_2CO_3 (2.33 g, 7.14 mmol), degassed water (2.4 ml) and 1 drop Aliquat® 336 was added. The reaction mixture was stirred at 90 °C for 72 hours. After cooling to room temperature the mixture was poured into 100 ml methanol and the polymer was allowed to precipitate. The polymer was filtered and purified by Soxhlet extraction using methanol, hexane and chloroform The chloroform phase was concentrated to a smaller volume in vacuum and precipitated in methanol (1:10). Filtration and drying in vacuum afforded **PMHTBT** as a dark red solid. Yield: 377 mg (88 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.67 – 8.49 (br, 1H), 8.07 (s, 1H), 7.92 (s, 1H), 1.83 – 0.99 (m, 12H), 0.98 – 0.77 (m, 3H). SEC ($CHCl_3$): M_w = 19400, M_n = 5000, PDI = 3.9.

Atomic force microscopy (AFM)

Figure S1. AFM topography images (5 µm × 5 µm) of solar cells based on blends of PCBM and (a) **P1**, S_a = 0.77 nm (b) **P2**, S_a = 0.94 nm (c) **P3**, S_a = 1.11 nm after thermocleavage.

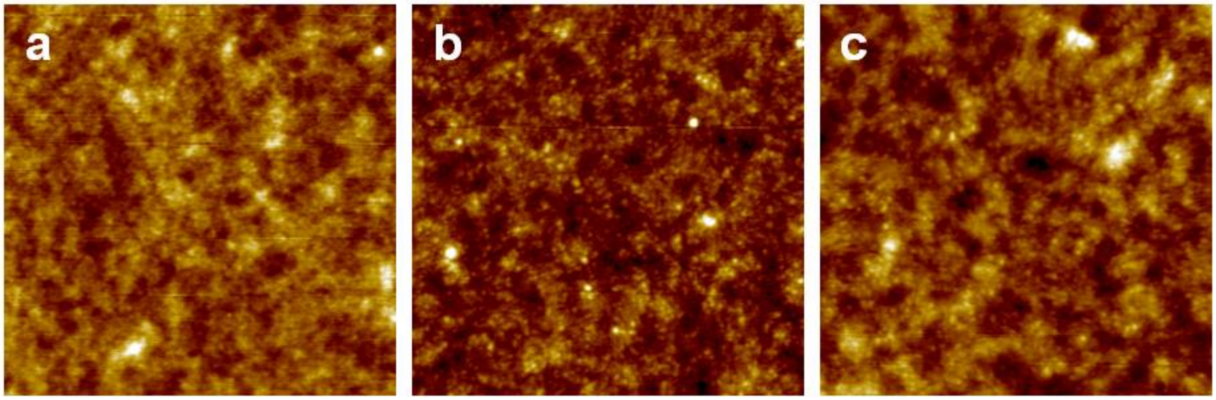


Table S1. The surface roughness of polymer/PCBM solar cells calculated at three positions on the surface of each sample using a 5 µm × 5 µm area.

Roughness parameter	**P1:PCBM**	**P2:PCBM**	**P3:PCBM**
$\mathbf{S_a}$	0.89 ±0.12	1.05 ±0.10	1.22 ±0.16
$\mathbf{S_q}$	1.21 ±0.21	1.40 ±0.17	1.57 ±0.19

Ultraviolet–visible spectroscopy (UV-vis)

Figure S2. UV-vis absorption spectra of **P1-P3** in thin films spin-coated on glass substrates and subsequently thermocleaved (conversion to **P0**) on a hotplate at 225 °C for 1 min. Thermocleaved films are indicated with an asterisk (*).

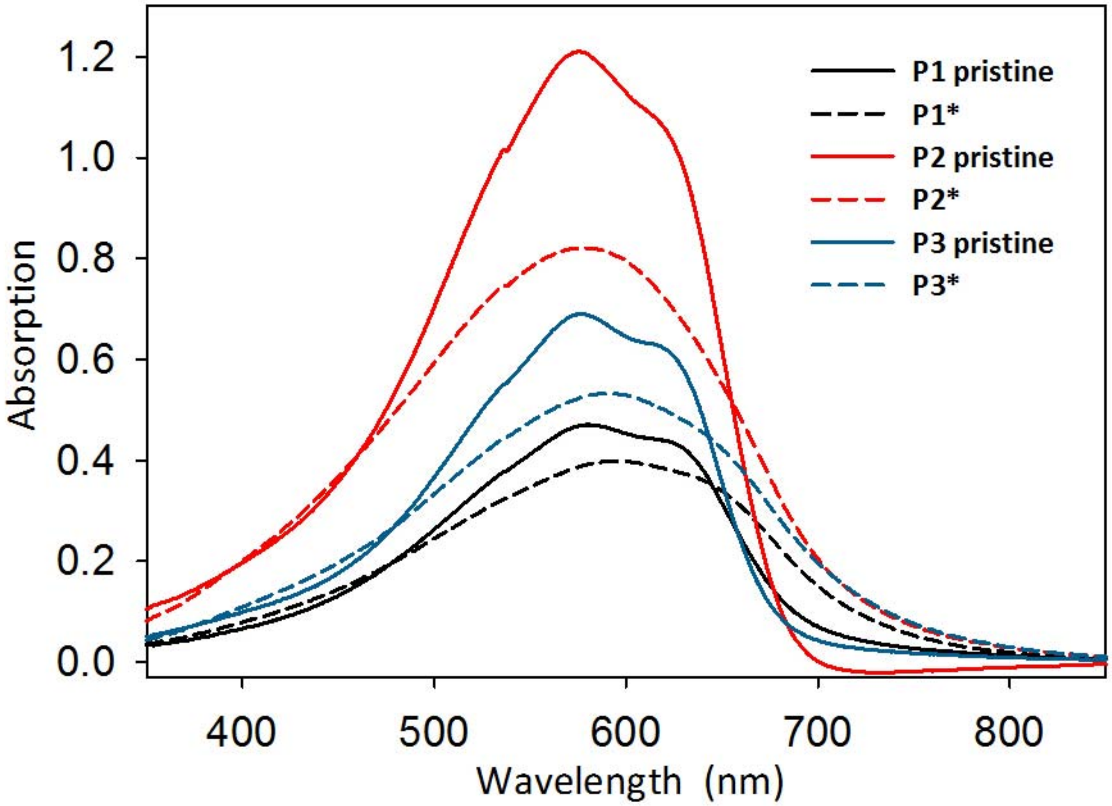


Figure S3. UV-vis absorption spectra of **P1** thin films spin-coated on glass substrates and then flashed (conversion to **P0**) at 35 mm distance from the lamp housing (power density aprrox. 6 kW/cm^2). Subsequently the samples were washed by immersion in ODCB for 5 min. Only the pristine **P1** sample washed off whereas the changes in the UV-vis were negligible for the flashed **P1** film.

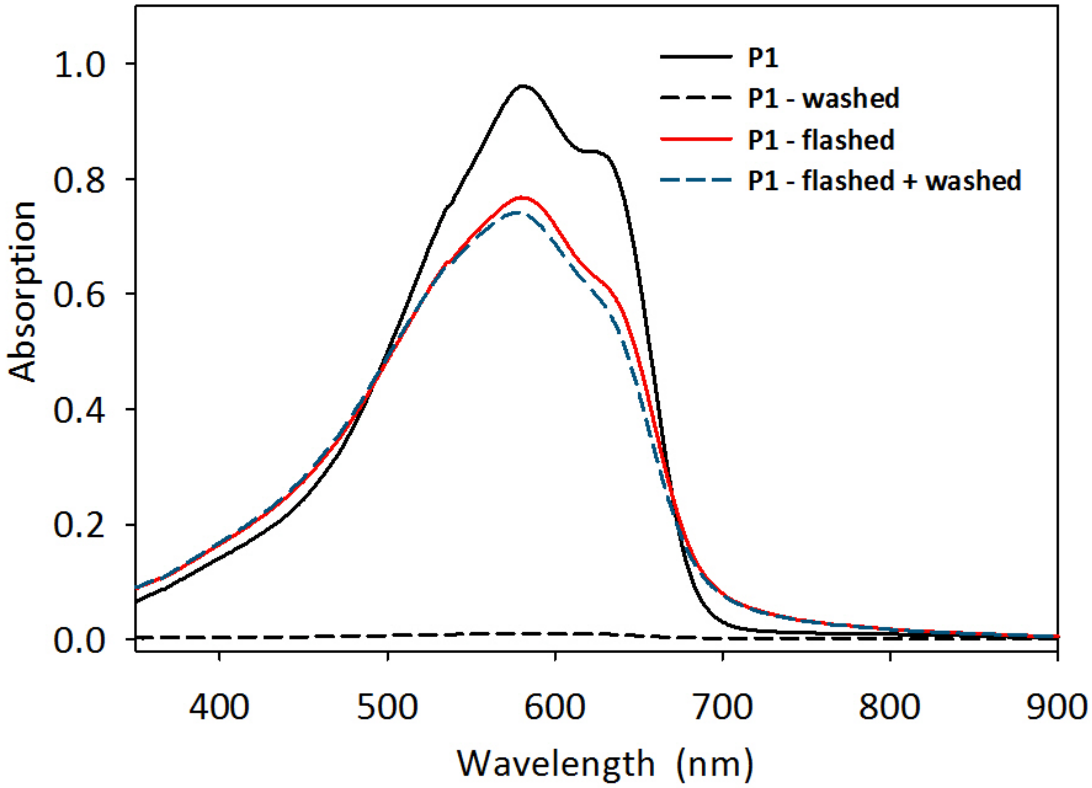
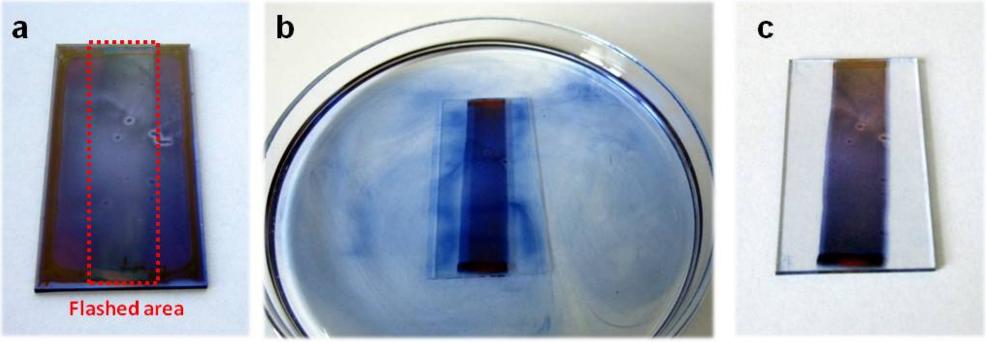


Figure S4. Photographic images of **P1** thin films according to figure S3. a) Flashed **P1** films were b) immersed into ODCB were un-flashed film areas was washed out, c) whereas flashed thermocleaved areas remained on the substrate demonstrating a high solvent resistance.



Thermogravimetric analysis (TGA)

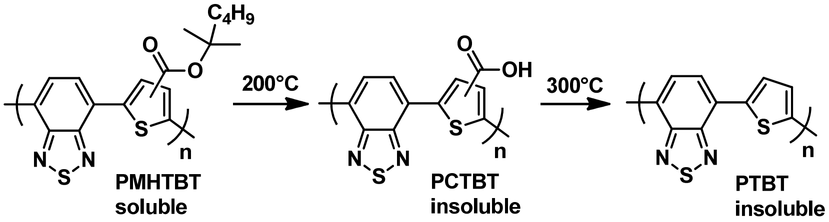
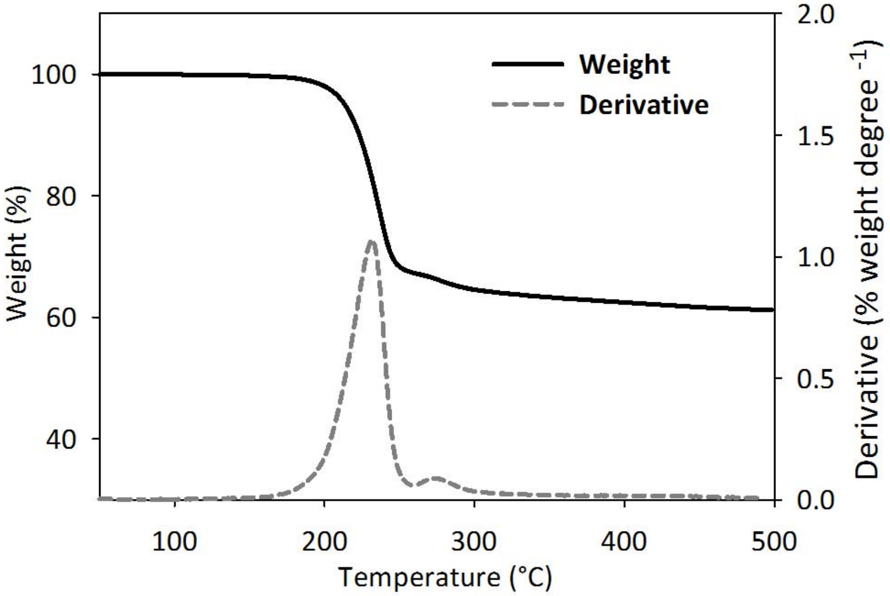
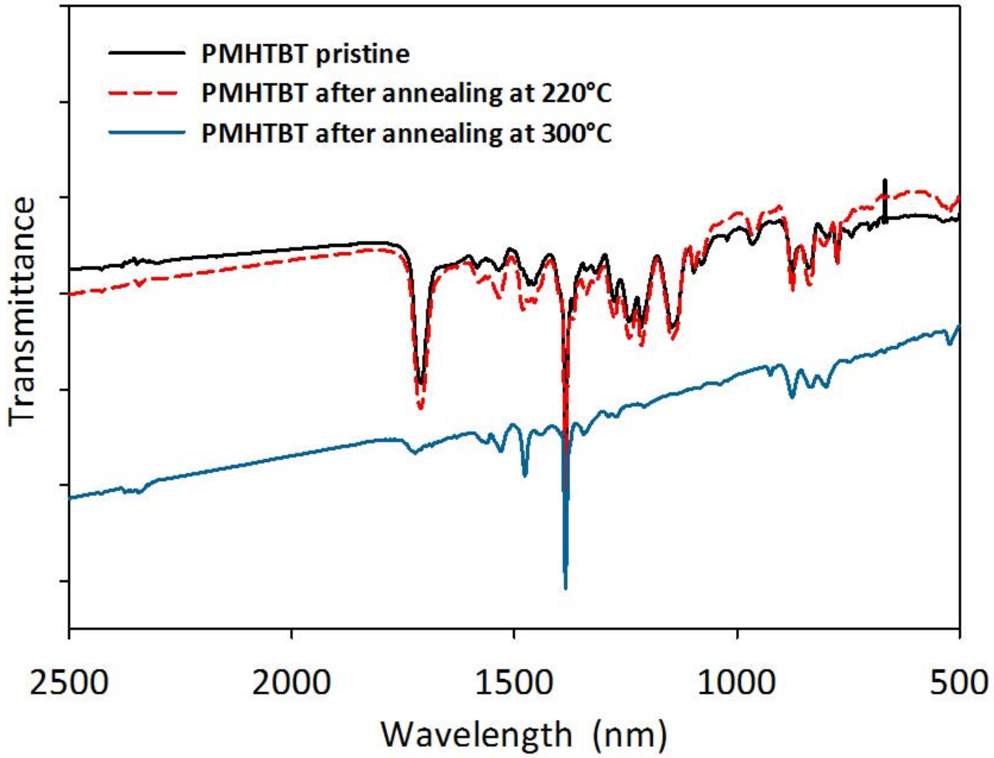


Figure S5. TGA of PMHTBT in the temperature range 50–500 °C. The TGA shows a ~36% weight loss in the 200-300°C range that corresponds well to elimination of the tertiary substituent and decarboxylation, as expected from earlier studies.[3]



Fourier-transform IR (FTIR)

Figure S6. FTIR spectra of PMHTBT films before annealing (black) after annealing at 220 °C (red) and after annealing at 300 °C (blue) for 5 min. One can observe that the absorption bands characteristic for ester and carboxylic acid moieties ($\nu_{C=O} \sim 1715$ cm^{-1} and $\nu_{C-O} \sim 1140\text{-}1280$ cm^{-1}) disappears after annealing at 300 °C which corresponds well to thermolytic transformation of PMHTBT to PTBT.



Supporting references

1 Helgesen, M.; Madsen, M. V.; Andreasen, B.; Tromholt, T.; Andreasen, J. W.; Krebs, F. C. *Polym. Chem.* **2011,** *2* (11), 2536-2542.

2 Krebs, F. C.; Fyenbo, J.; Jørgensen, M. *J. Mater. Chem.* **2010,** *20* (41), 8994-9001.

3 Bjerring, M.; Nielsen, J. S.; Nielsen, N. C.; Krebs, F. C. *Macromolecules* **2007,** *40* (16), 6012-6013.