Supporting Information

Nanoporous poly(3-hexylthiophene) thin films based on "click" prepared degradable diblock copolymers

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Materials. 3-Hexylthiophene (Acros, 98%), 4-pentynoic acid (Acros, 98%), iodine (Acros, 99.5%), iodobenzene diacetate (Acros, 98%), isopropylmagnesium chloride solution (iPr-MgCl, Acros, solution 2.0M in THF), phosphorus oxychloride (Aldrich, 99%), sodium borohydride (Aldrich, 98%), copper (I) bromide (Aldrich, 99.999%), N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), pyridinium p-toluenesulfonate (Aldrich, 98%), poly(ethylene glycol) methyl ether (mPEG, 2000 and 5000g/mol, Aldrich), sodium azide (Fluka, 99%), 4-dimethylaminopyridine (DMAP, Merck, 99%), N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC, Merck, 99%), hexane (Fisher Chemicals, 99%), acetone (Fisher Chemicals, 99%), isopropanol (Fisher Chemicals, 99%) and methanol (Fisher Chemicals, 99%) were used as received. N-Bromosuccinimide (Across, 99%) was recrystallized from water before use. Ni(dppp)Cl_2 (dppp = propane-1,3-diylbis(diphenylphosphine)) (Acros Organics, 99%) was stored under nitrogen in a glovebox. Chloroform (Fisher Chemicals, 99%), dichloromethane (Fisher Chemicals, 99%) and N,N-dimethylformamide (Aldrich, 99%) were dried over diphosphorus pentaoxide and distilled. Toluene (Fisher Chemicals, 99%) and tetrahydrofuran (Fisher Chemicals, 99%) were dried over sodium benzophenone and distilled. Column chromatographies were performed using Merck 60 silica gel 70-230 mesh and Fluka activated neutral aluminum oxide as adsorbents. All reactions were performed in flame-dried glassware under purified nitrogen.

Apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance- DRX 250 and II+600 apparatuses at room temperature in $CDCl_3$ at sample concentration (10-30mg/0.6mL). All chemical shifts and coupling constants are reported in ppm and Hz, respectively. Size exclusion chromatography (SEC) was performed on a Agilent Technologies 1200 chromatograph equipped with a degasser, an isocratic HPLC pump, an autosampler, a RI (refractive index) detector and three columns: a guard column PL gel 5 µm and two columns PL gel mixed-D 5 µm. Tetrahydrofuran (THF) at 35°C was used as a mobile phase at a flow rate 1mL/min, sample concentration was 1mg/mL and SEC was calibrated with polystyrene standards. Ultraviolet-Visible (UV-VIS) absorption spectra were taken on a DU 800 (Beckman Coulter) spectrometer from 300 to 800 nm. Fourier transform infrared (FTIR) spectra were recorded from 600 to 4000 cm^{-1} using an IRAffinity-1 (Shimadzu) spectrometer. MALDI-ToF mass spectra were measured on a Waters QToF Premier mass spectrometer equipped with a nitrogen laser, operating at 337 nm with a maximum output of 500 $mJ.m^{-2}$ delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight mass analyses were performed in the reflectron mode at a resolution of about 10.000 and the samples were analyzed using trans-2-[3-(4-tertbutylphenyl)-2-methylprop-2-enylidene]-malonitrile (DCTB), as a matrix at 40 mg/ml solution in $CHCl_3$.[1] Differential scanning calorimetry (DSC) measurements were acquired on a temperature modulated DSC Q2000 apparatus equipped

with an autosampler from TA Instruments under nitrogen flow at heating rate 10°C/min from -80 to 225°C. Grazing Incidence X-ray diffraction (GIXRD) morphological analyses were performed on Siemens D5000 diffractometer using Cu Kα radiation with wavelength (40 kV/30 mA, 1.5406 Å) at room temperature. The samples were step-scanned in the range from 4 to 50° in 2θ with step size of 0.1° and step time of 4 s. The angle of incidence α was set at 3°. XPS measurements were carried out in the UHV chamber of an ESCALAB-MkII (VG Scientific) electron spectrometer using Mg Ka excitation with a total instrumental resolution of ~ 1 eV. Energy calibration was performed taking the C1s line at 285 eV as a reference. Surface atomic concentrations were evaluated using Scofield's ionization cross-sections with no corrections for l (the mean free path of photoelectrons) and the analyzer transmission function. The experimental values for the element atomic percentages obtained from the XPS analysis are the average of three independent measurements. The high-resolution spectra were dissected by means of a special deconvolution software package. Atomic Force Microscopy (AFM) images were obtained with a Nanoscope V microscope from Veeco operating in tapping mode. Microfabricated silicon cantilevers with a spring constant of ~40 $N.m^{-1}$ were used and the image analysis was processed with Nanoscope v7.20 software.

Synthesis of regioregular head-to-tail poly(3-hexylthiophene) (P3HT, Mn=8000) with Bromine/Hydrogen end groups. GRIM polymerization was performed in a 250 ml two-neck round bottom flask where 2-bromo-3-hexyl-5-iodothiophene (4.48 g, 12.00 mmol) was charged under nitrogen atmosphere. After three azeotropic distillations by toluene, anhydrous THF (75 ml) was added via a syringe and the solution was cooled down to 0°C. *i*Pr-MgCl (2.0 M solution in THF, 6 mL, 12.00 mmol) was added via a syringe and the mixture was stirred at 0°C for 0.5 h. That mixture was transferred via cannula to a flask containing a suspension of $Ni(dppp)Cl_2$ (135.5 mg, 0.25 mmol) in THF (75.0 ml) calculated for the preparation of a P3HT with Mn of 8000 g/mol. The polymerisation was carried out in a cold room at 5-10°C for 24 h and was quenched by rapid addition of 5N HCl. After termination, the reaction was stirred for 0.5h before precipitation in cold methanol. The product was washed with methanol and hexane to afford a purple solid (1.55 g, yield 78 %); >95% rr-P3HT; ^{1}H-NMR ($CDCl_3$, δ ppm): 6.97 (s, 1H), 2.79 (t, J=6.8Hz, 2H), 1.78-1.64 (m, 2H)), 1.50-1.36 (m, 2H), 1.36-1.25 (m, 4H), 0.90 (t, J=6.8Hz, 3H); ^{13}C-NMR ($CDCl_3$, δ ppm): 140.0, 133.9, 130.7, 128.8, 31.9, 30.7, 29.7, 29.5, 22.9, 14.4; FT-IR (cm^{-1}): 724, 819, 1376, 1454, 1510, 1562, 2854, 2923, 2953; UV-VIS ($CHCl_3$, λ nm): 451; MALDI-ToF: mainly Br/H end-capped, m/z = 166*n+79(Br)+1(H); M_n(SEC)= 8200 g/mol, $Đ_M$= 1.06.

Modification of regioregular head-to-tail poly(3-hexylthiophene) (P3HT, Mn=8200) to alkynyl end-functionalised macroreagent (P3HT–C≡CH). The modification procedure of the P3HT macroinitiator was carried out in three steps. At the first step, the hydrogen group of Br/H terminated P3HT homopolymer was converted to an aldehyde group via a Vilsmeier-Haack reaction

to afford the expected Br/CHO terminated poly(3-hexylthiophene). Briefly, Br/H end-capped P3HT (Mn= 8200, $Đ_M$= 1.06, 500 mg, 0.061 mmol) was dissolved in anhydrous toluene (~ 250 ml) under inert atmosphere. N,N-dimetylformamide (DMF) (1.9 ml, 24.4 mmol, ~ 400 equiv. excess) and phosphorus oxychloride ($POCl_3$) (2.2 ml, 24.4 mmol, ~ 400 equiv. excess) were then added to the solution. The temperature was increased and reaction was stirred at 75°C for 24 h. The solution was cooled down to room temperature and 20 ml of a sodium acetate saturated aqueous solution was added carefully to quench the reaction. The mixture was stirred for another 4 h, poured in cold methanol, filtrated, extracted with 3x50 ml portions $CHCl_3$ from water and dried. At the second step, the aldehyde group was reduced to methylol group via selective reduction using sodium borohydride ($NaBH_4$) to produce the Br/CH_2OH terminated poly(3-hexylthiophene). Shortly, Br/CHO end-capped P3HT (480 mg, 0.059 mmol) was dissolved in anhydrous THF (250 ml) under inert atmosphere. $NaBH_4$ (powder) (0.0179 g, 0.472 mmol, ~ 8 equiv. excess) was then added at 0°C to the solution. The temperature was increased and the medium was stirred at room temperature for 1 h 30 min. The solvent was then evaporated and 10 ml of 2.5N HCl was added to quench the excess of $NaBH_4$. The obtained polymer was finally washed with water (2x80 ml), methanol (2x80 ml), filtered and dried. At the third step the methylol end group of Br/CH_2OH terminated poly(3-hexylthiophene) was esterified with 4-pentynoic acid leading to the expected alkynyl end-functionalized macroinitiator (Br–P3HT–C≡CH). Briefly, the Br/CH_2OH end-capped P3HT (200 mg, 0.024 mmol, 1 eq) was dissolved in dry $CHCl_3$ (20 ml) under inert atmosphere. Pentynoic acid (188 mg, 1.92 mmol, 80 eq) was added at room temperature to the above solution, followed by EDC (368 mg, 1.92 mmol, 80 eq) and then DMAP (88 mg, 0.72 mmol, 30 eq). The medium was stirred for 24 h, followed by a dilution with 40 ml of $CHCl_3$ and finally extracted with 2x50 ml of H_2O. The organic phase was dried over $MgSO_4$, filtered and the solvent was evaporated. The product was redisolved in 10 ml of THF and precipitated into 100 ml of chilled methanol. Finally, the precipitated product was filtered and washed well with acetone and hexane. Yield: 96 %; ^{1}H-NMR ($CDCl_3$, δ ppm): 6.99 (s, 1H), 5.26 (s, signal of small intensity for -$CH_2OC(O)$- group), 2.81 (t, J=6.8Hz, 2H), 1.98 (t, J=2.5Hz, signal of small intensity for terminal –C≡CH group), 1.78-1.64 (m, 2H), 1.50-1.25 (m, 6H), 0.93 (t, J=6.8Hz, 3H); Mn (NMR)=7450; MALDI-ToF: mainly Br/$CH_2OC(O)(CH_2)_2$C≡CH end-capping group, m/z= 166*n+79(Br)+111($C_6H_7O_2$); Mn(SEC)= 8450 g/mol; $Đ_M$= 1.18.

Synthesis of PEO macroreagent containing cleavable acetal and clickable azide terminal group (PEO2000 azide). PEO monomethyl ether (1.20 g, 0.60 mmol, Mw=2000) and pyridinium *p*-toluenesulfonate (15.1 mg, 0.06 mmol) were introduced in a flask under N_2 atmosphere. After three azeotropic distillations by toluene, dry CH_2Cl_2 (7 mL) was added and the solution was cooled down to 0°C. 2-Chloroethyl vinyl ether (3.0 mmol, 305 μL) was added dropwise at that temperature

and then it slowly increased. The reaction medium was stirred at 25°C for 1 h under N_2 atmosphere. The obtained reaction mixture was quenched by adding 5 wt% of basic Na_2CO_3 aqueous solution (~ 30 mL), diluted with another 50 mL of CH_2Cl_2, washed with 50 mL of water and 2x50 mL portions of brine. All aqueous layers were further extracted with 40 mL of CH_2Cl_2 and the combined CH_2Cl_2 solutions were dried over $MgSO_4$ and evaporated to dryness under reduced pressure. The product was redissolved in 10 mL of a CH_2Cl_2/THF (1/1: v/v) mixture and precipitated into 100 mL of a cold mixture of hexane and diethyl ether (1/1: v/v) to give PEO2000 acetal with terminal Cl group (1.17 g, yield 97.5%); ^{1}H-NMR ($CDCl_3$, δ ppm): 4.82 (q, J=5.4Hz, 1H, H_3C-C*H*(OR)(OR')), 3.80-3.50 (m, 180H, -OCH_2CH_2O-), 3.37 (s, 3H,CH_3O-PEO, 1.33 (d, J=5.4Hz, 3H, H_3C-CH(OR)(OR')).

The as-obtained PEO acetal (0.6 g, 0.3 mmol, Mw=2000) and NaN_3 (195 mg, 3.0 mmol) were then dissolved in ~ 3 ml of anhydrous N,N-dimetylformamide (DMF) under inert atmosphere. The temperature was increased and reaction was stirred at 120 °C for 3 h. The solution was concentrated under reduced pressure on rotary evaporator, diluted with 30 mL of CH_2Cl_2, washed with 50 mL of water and 2x50 mL portions of brine. All aqueous layers were further extracted with 30 mL of CH_2Cl_2 and the combined CH_2Cl_2 solutions were dried over $MgSO_4$ and evaporated to dryness under reduced pressure. The product was redissolved in 10 mL of a mixture of CH_2Cl_2 and THF (1/1:v/v) and precipitated into 100 mL of a cold hexane/diethyl ether mixture (1/1:v/v). The product was further filtrated and washed well with Et_2O to give PEO carrying a cleavable acetal and clickable azide terminal group (PEO2000 azide) (0.54 g, yield 90.0 %); ^{1}H-NMR ($CDCl_3$, δ ppm): 4.81 (q, J=5.4Hz, 1H, H_3C-C*H*(OR)(OR')), 3.80-3.50 (m, 180H, -OCH_2CH_2O-), 3.43-3.35 (m, 2H, N_3CH_2CH_2O-), 3.37 (s, 3H,CH_3O-PEO, 1.33 (d, J=5.4Hz, 3H, H_3C-CH(OR)(OR')); M_n(SEC)= 3000 g/mol, $Đ_M$= 1.09.

Synthesis of PEO macroreagent containing cleavable acetal and clickable azide terminal group (PEO5000 azide). The general procedure used for the preparation of the PEO5000 azide macroreagent is the same as described above for PEO2000 azide. Yield = 91.6 %, ^{1}H-NMR ($CDCl_3$, δ ppm): 4.82 (q, J=5.4Hz, 1H, H_3C-C*H*(OR)(OR')), 3.80-3.50 (m, 450H, -OCH_2CH_2O-), 3.43-3.35 (m, 2H, N_3CH_2CH_2O-), 3.37 (s, 3H,CH_3O-PEO, 1.33 (d, J=5.4Hz, 3H, H_3C-CH(OR)(OR')); M_n(SEC)= 8350 g/mol, $Đ_M$= 1.08.

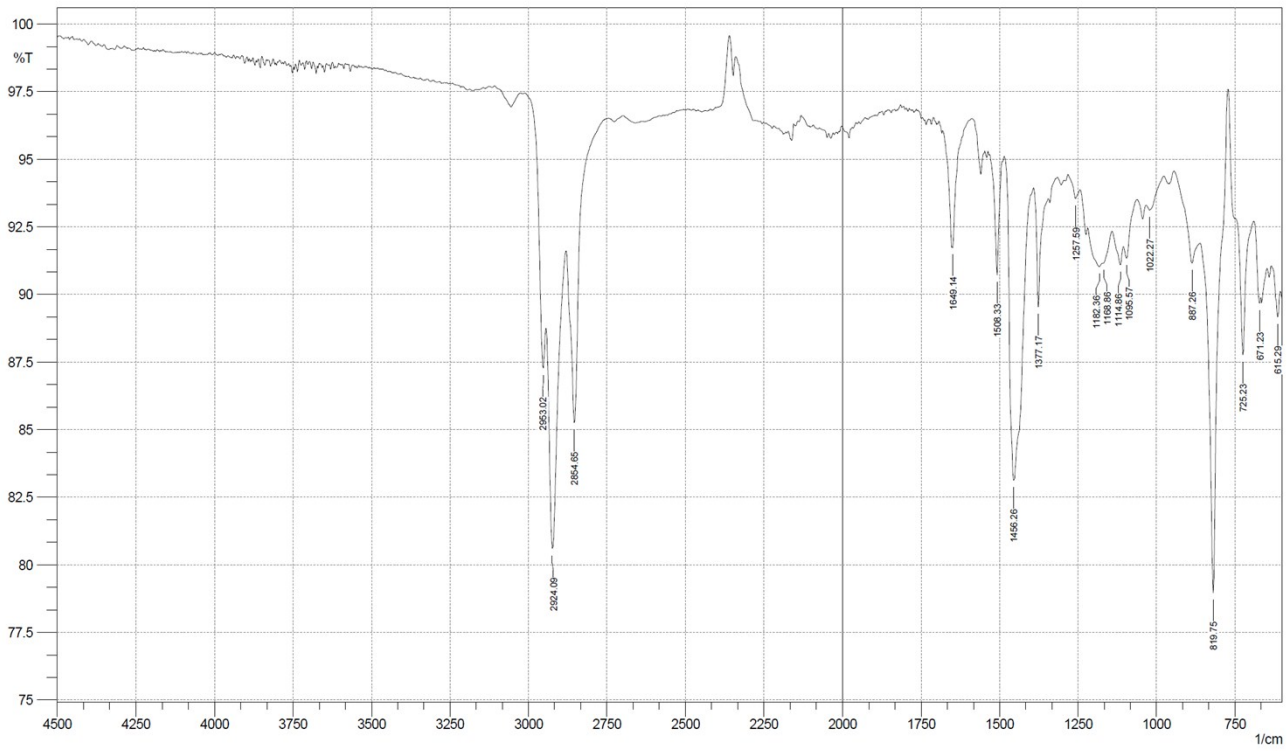

Figure S1. FTIR analysis of P3HT homopolymer with Br/CHO end-groups;

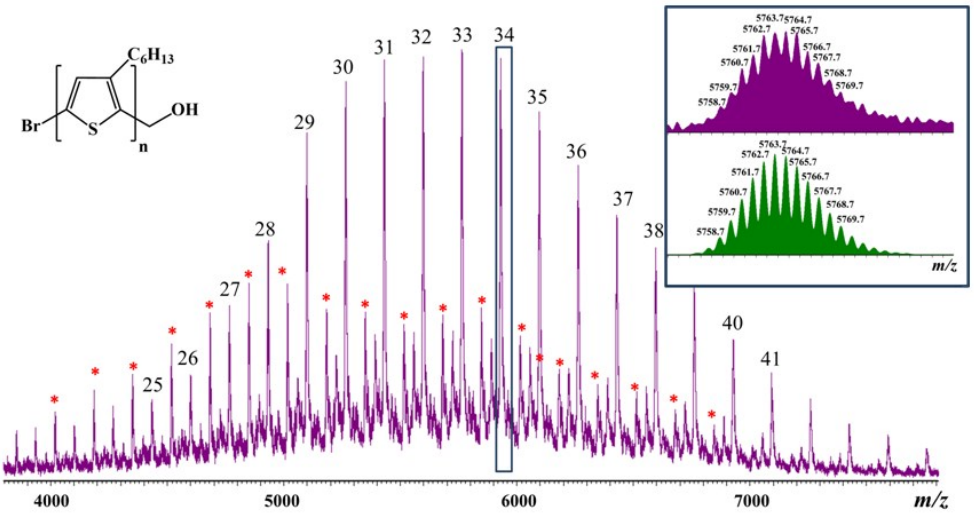

Figure S2. MALDI mass spectrum recorded for P3HT-OH. The number at the top of each signal corresponds to the number of monomer units. The inset corresponds to a comparison between the theoretical isotopic distribution (bottom) and the experimental one (above). By asterisk (*) is assigned the adduct obtained from the expected polymer and one molecule of matrix (DCTB).

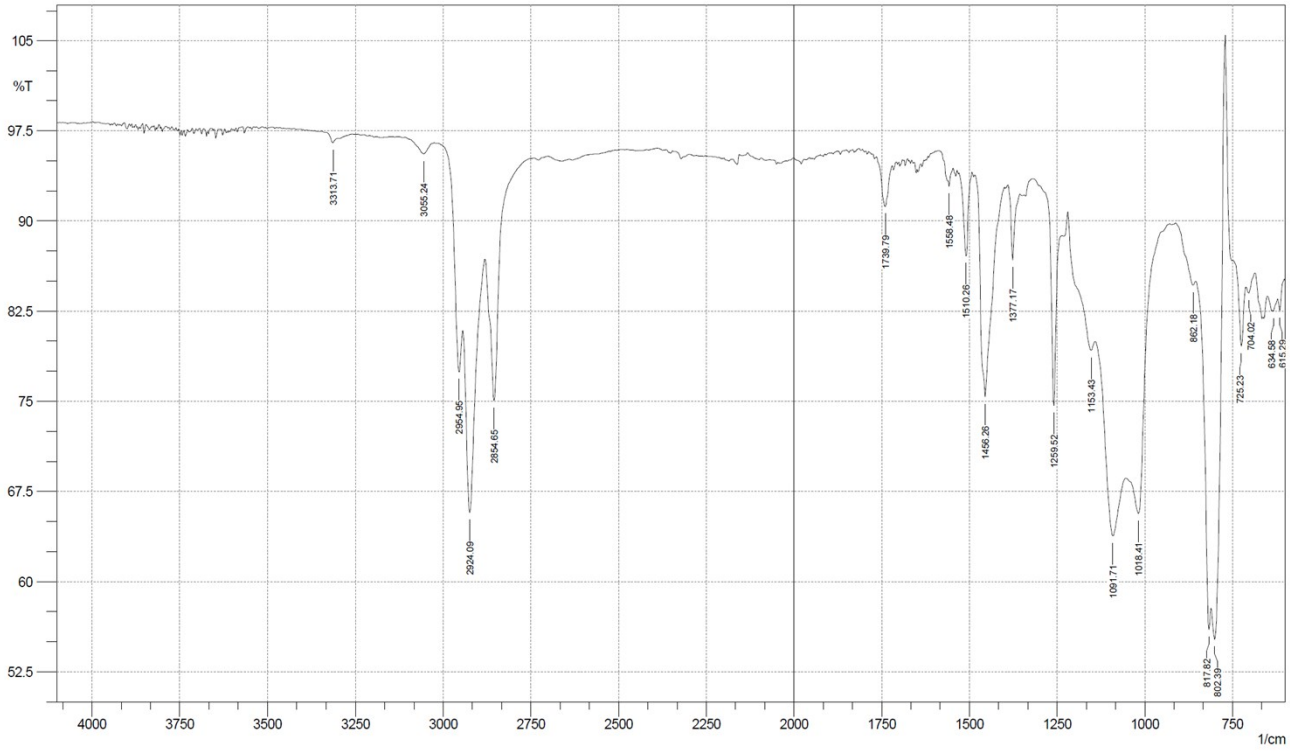

Figure S3. FTIR analysis of P3HT macroreagent with Br/C≡CH end-groups;

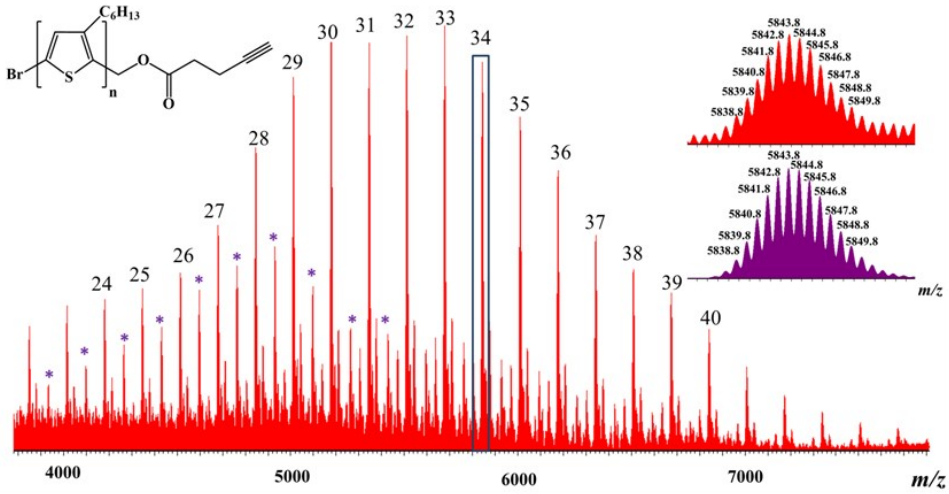

Figure S4. MALDI mass spectrum recorded for P3HT-C≡CH. The number at the top of each signal corresponds to the number of monomer units. The inset corresponds to a comparison between the theoretical isotopic distribution (bottom) and the experimental one (above). By asterisk (*) is assigned the adduct obtained from the expected polymer and one molecule of matrix (DCTB).

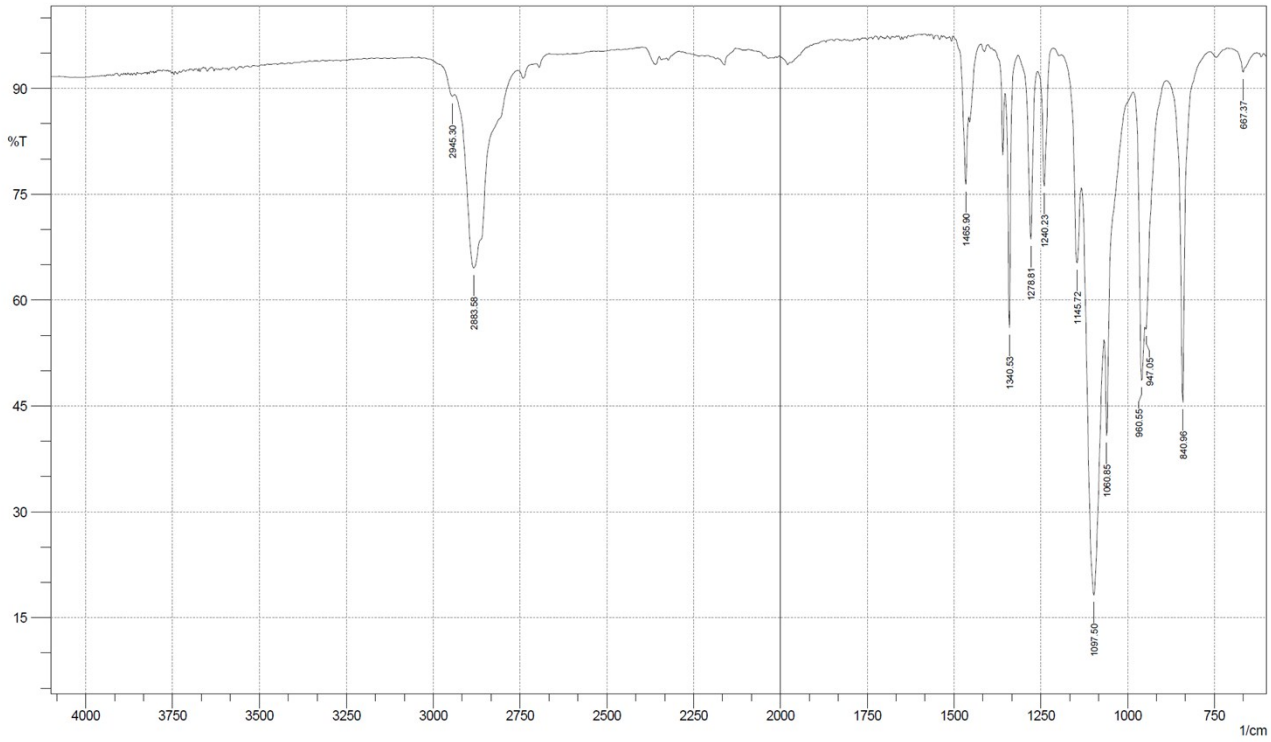

Figure S5. FTIR analysis of PEO macroreagent with acetal and Cl end-group;

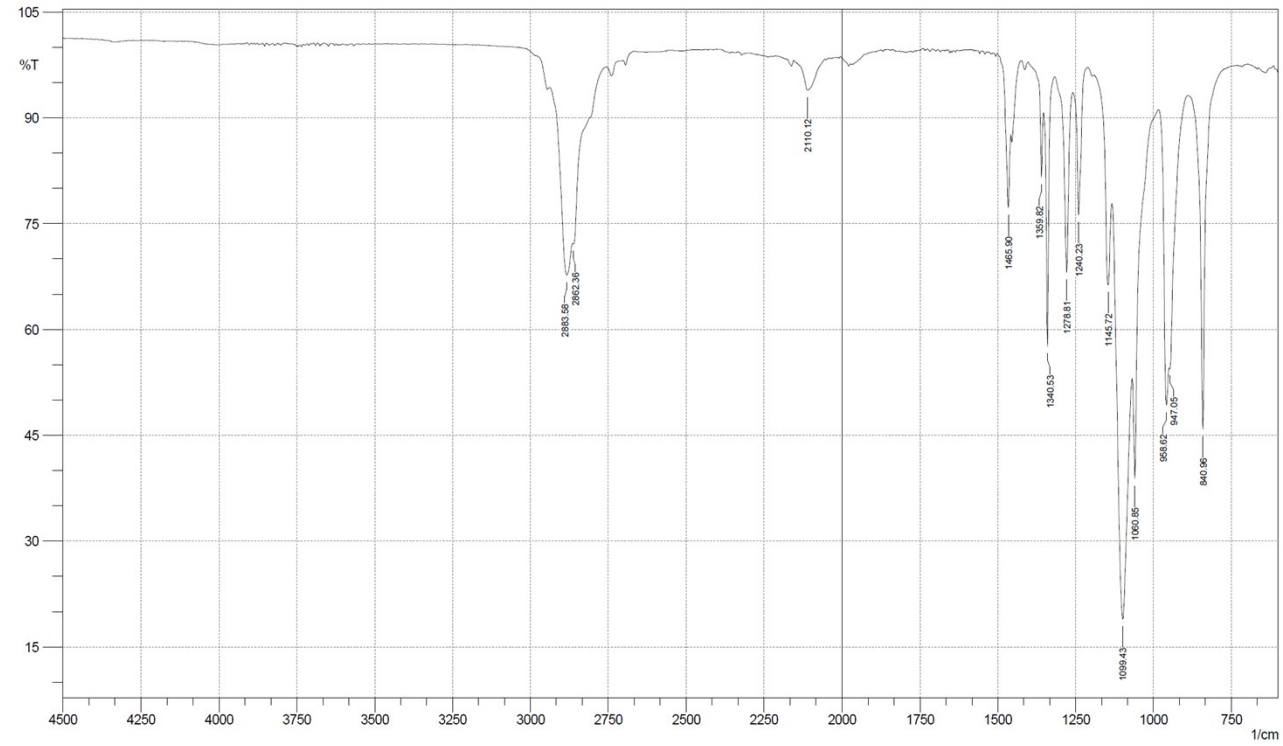

Figure S6. FTIR analysis of PEO macroreagent with N_3 end-group;

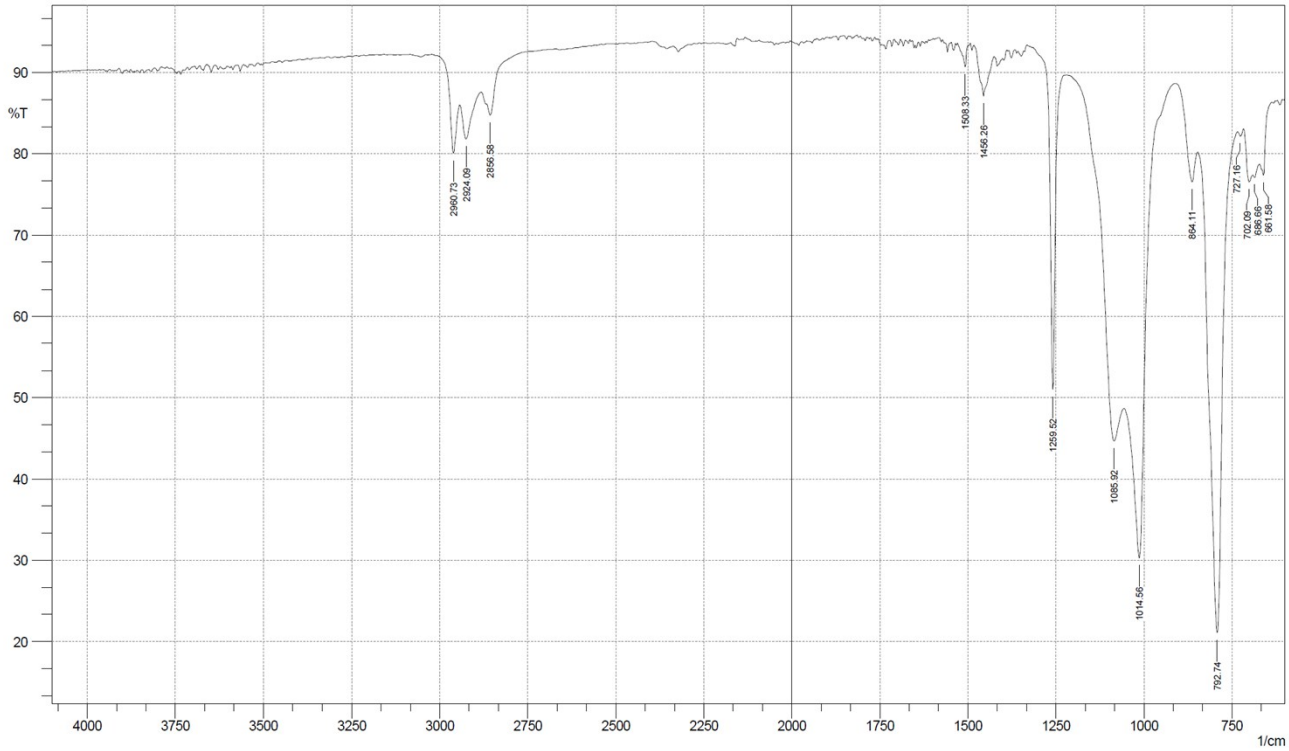

Figure S7. FTIR analysis of P3HT-b-PEO2000 copolymer;

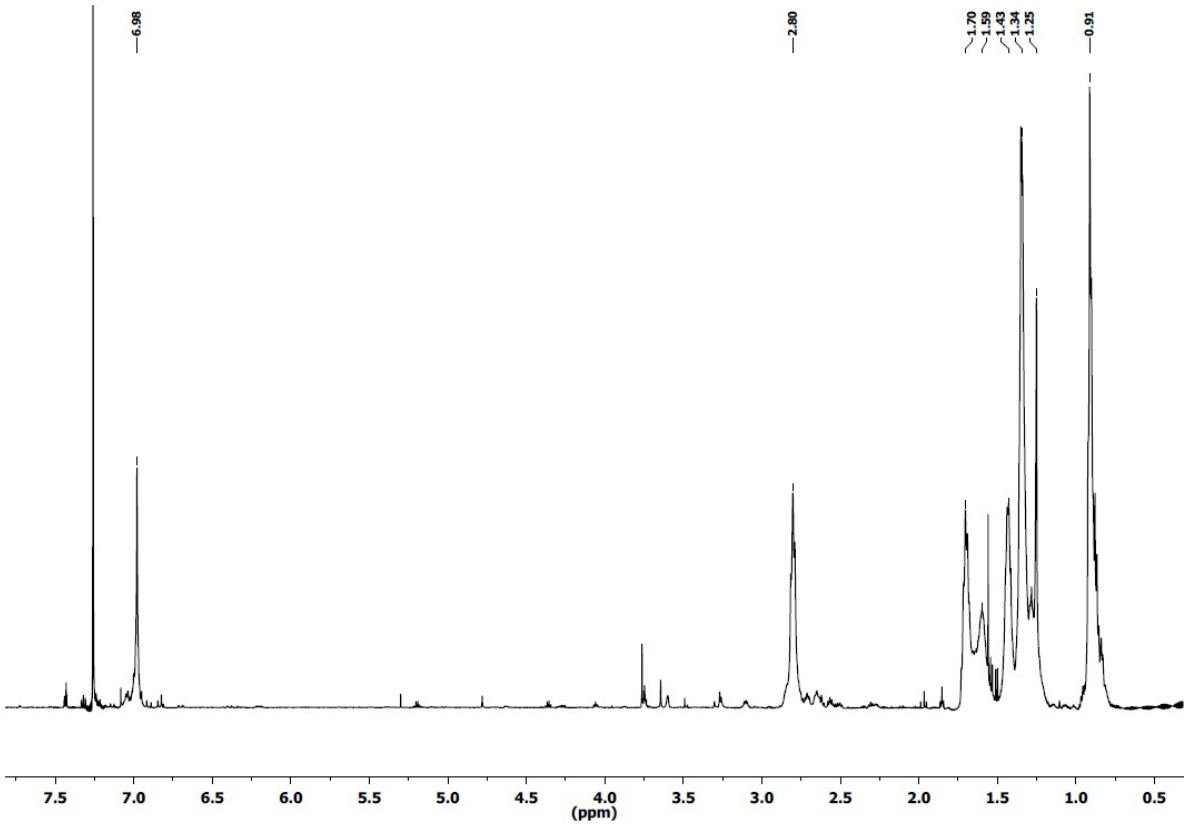

Figure S8. ^{1}H NMR spectrum of separated product after degradation of P3HT-b-PEO5000 copolymer matching the one of P3HT block;

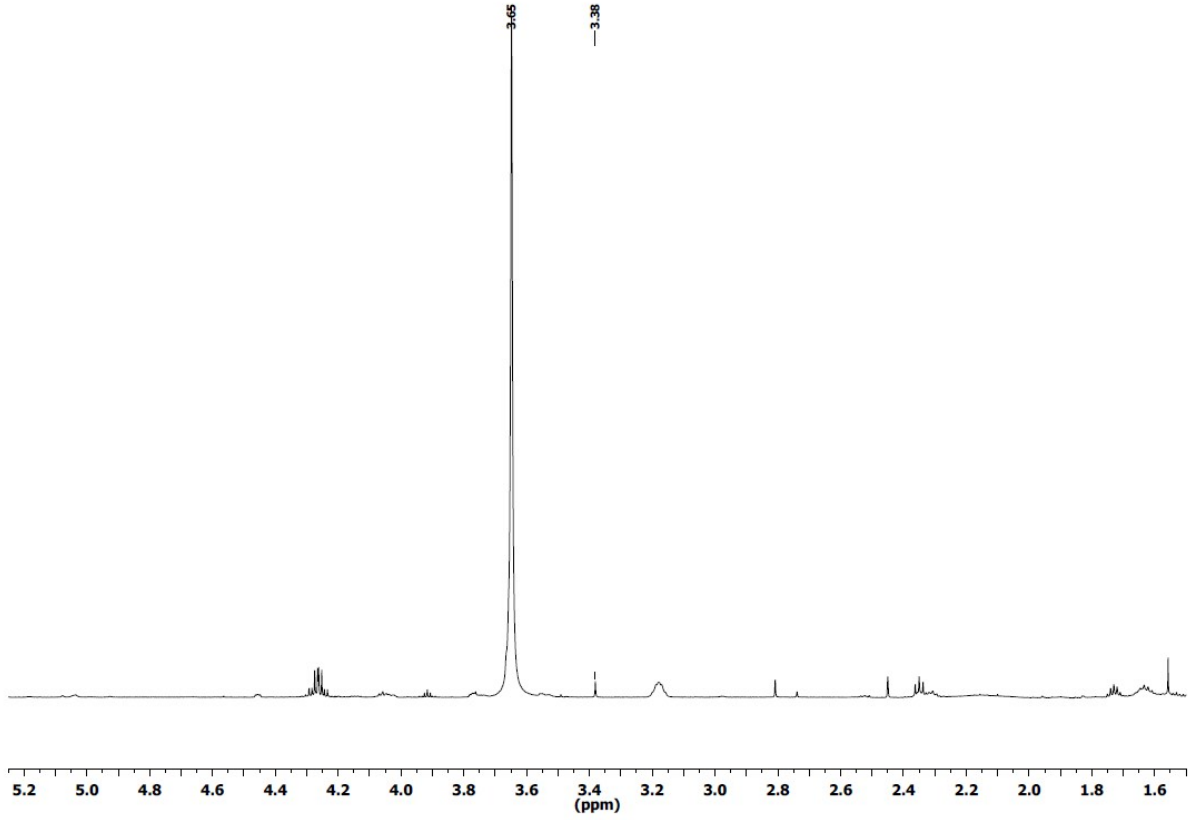

Figure S9. ^{1}H NMR spectrum of separated product after degradation of P3HT-b-PEO5000 copolymer matching the one of PEO5000 block;

References

1. J. De Winter, G. Deshayes, F. Boon, O. Coulembier, P. Dubois and P. Gerbaux, *J. Mass Spectrometry*, 2011, **46**, 237.