Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Effect of molecular weight on the properties and organic solar cell device performance of a donor-acceptor conjugated polymer

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General Experimental Information

Unless noted, all materials were reagent grade and used as received without further purification. Chromatographic separations were performed using standard column methods with silica gel (Merck 9385 Kieselgel 60). Thin layer chromatography was performed on Merck Kieselgel 60 silica gel on glass (0.25 mm thick).

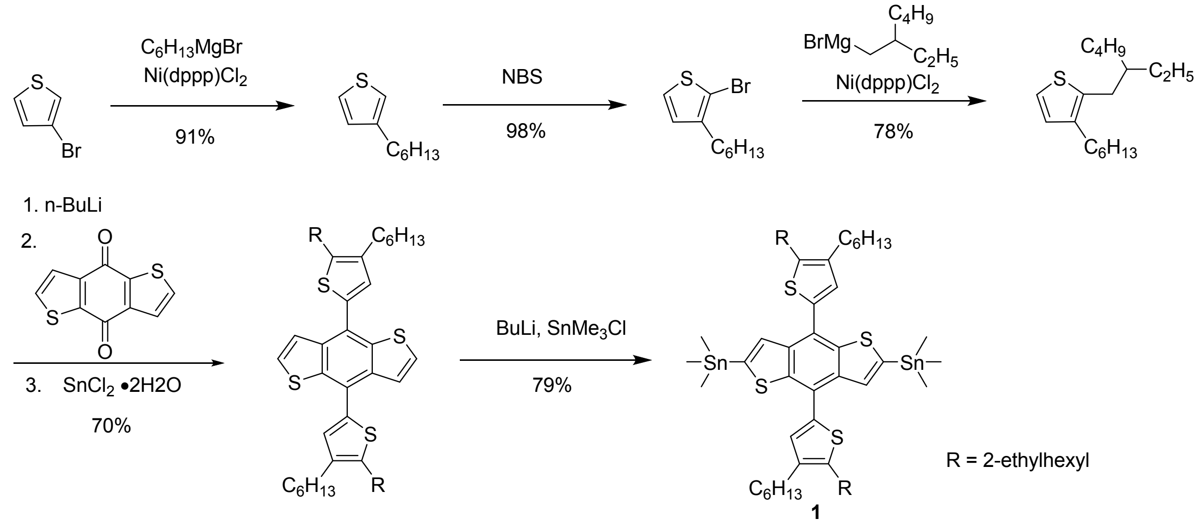
Infrared (IR) spectra were obtained on a Perkin Elmer Spectrum One FT-IR spectrometer and UV-vis spectra were recorded using a Cary 50 UV-Vis spectrometer. Photoluminescence was measured with a Varian Cary Eclipse fluorimeter. Melting points were determined on a Büchi 510 melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were carried out on a 400 MHz spectrometer. All NMR data was referenced to the chloroform signal and peak multiplicity was reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublets of doublets, m = multiplet, br = broad). Differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer Sapphire DSC.

Gel permeation chromatography (GPC) data was obtained using a Viscotek GPC Max VE2001 solvent/sample module equiped with a Viscotek VE3580 refractive index detector. Toluene was used as the eluent with a 200 µl sample volume injection. Samples were passed through three 30 cm, PL gel (5 µm) mixed C columns and one 30 cm, PL gel (3 µm) mixed E column at 0.6 ml/min. Molecular mass distributions were calculated relative to narrow polystyrene reference standards.

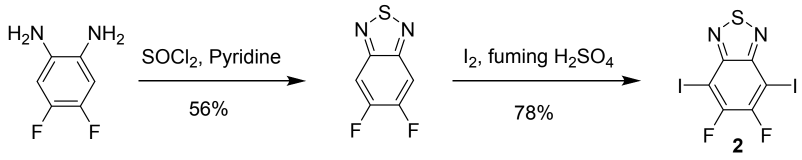
High temperature gel permeation chromatography (HT-GPC): Molecular weights of polymer were characterized by HT-GPC performed in 1,2,4-trichlorobenzene (TCB) with 500 ppm 3,5-di-tert-butyl-4-hydroxytoluene (1.0 mL/min) at 120°C using a Malvern Viscotek 350A HT-GPC system with a Refractive Index Detector, a Viscotek 2600 Photodiode Array Detector, a Viscometry Detector, a series of four Malvern high temperature columns (1×Guard + 3×HT6000M), and OmniSEC Software. The GPC was calibrated with narrow polydispersity polystyrene standards (Malvern PolyCal PS standards, MW from 1050 to 4.2×10^{6}), and molecular weights are reported both as polystyrene equivalents based on the refractive index detector, and absolute values using universal calibration based on a combination of the refractive index detector and the viscosity detector. The sample was dissolved in TCB with 500 ppm BHT at a concentration around 2.5 mg/mL at 120 °C for 2 hours before injection.

Cyclic voltammetry (CV) experiments were performed at a sweep rate of 100 mV/s. CVs were carried out in a three-electrode cell consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and a Ag/Ag^{+} pseudo-reference electrode. The supporting electrolyte was 0.10 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in CH_3CN. The solutions were deoxygenated by sparging with argon prior to each scan and blanketed with argon during the scans. The glassy carbon working electrode was prepared by polishing with 5 mm alumina and washed and dried before the polymer was drop-casted on the electrode from chlorobenzene solution to form a film. Ferrocene/ferroceium redox couple was used as the internal standard. The HOMO energy level was calculated from the onset of the oxidation potential of the polymer using the following: $E_{HOMO} = -(4.8 + E_{ox}\text{ onset})$ eV.

Monomer synthesis

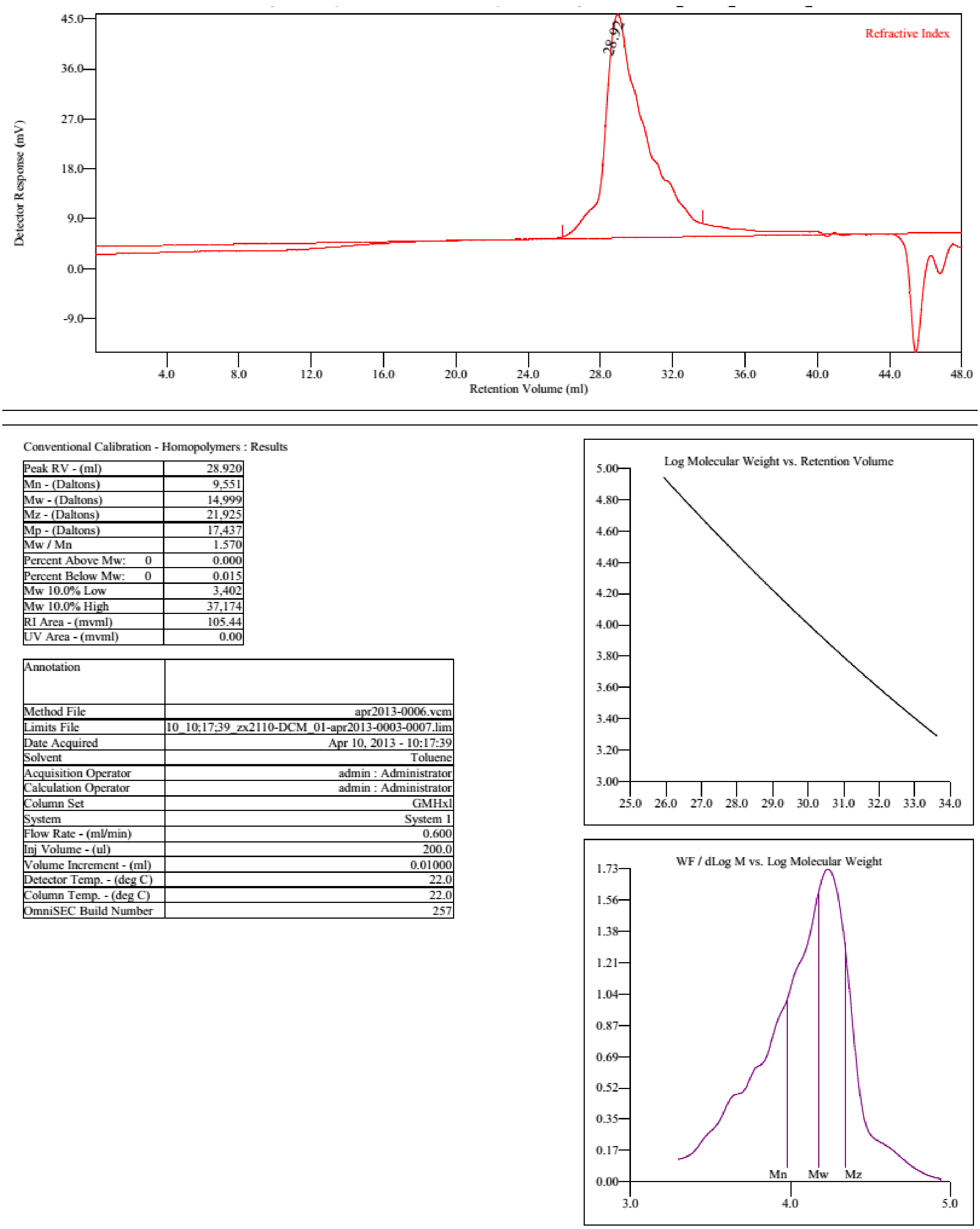


Monomer **1** was synthesized following previously reported procedure (T. Qin, W. Zajaczkowski, W, Pisula, *et al. J. Am. Chem. Soc.,* 2014, 136, 6049-6055) except that the bistrimethyltin compound **1** was purified by recrystallization from isopropanol / dichloromethane at 5 °C. The NMR and characterization data are in accordance with literature.



Monomer 2 was synthesized following literature reported by You (H. Zhou, L. Yang, A. C. Stuart, S. C. Price, S. Liu and W. You, *Angew. Chem. Int. Ed.*, 2011, 50, 2995-2998).

Polymer Characterization Data



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	28.920
Mn - (Daltons)	9,551
Mw - (Daltons)	14,999
Mz - (Daltons)	21,925
Mp - (Daltons)	17,437
Mw / Mn	1.570
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.015
Mw 10.0% Low	3,402
Mw 10.0% High	37,174
RI Area - (mvml)	105.44
UV Area - (mvml)	0.00

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Volume Increment - (ml)	0.01000
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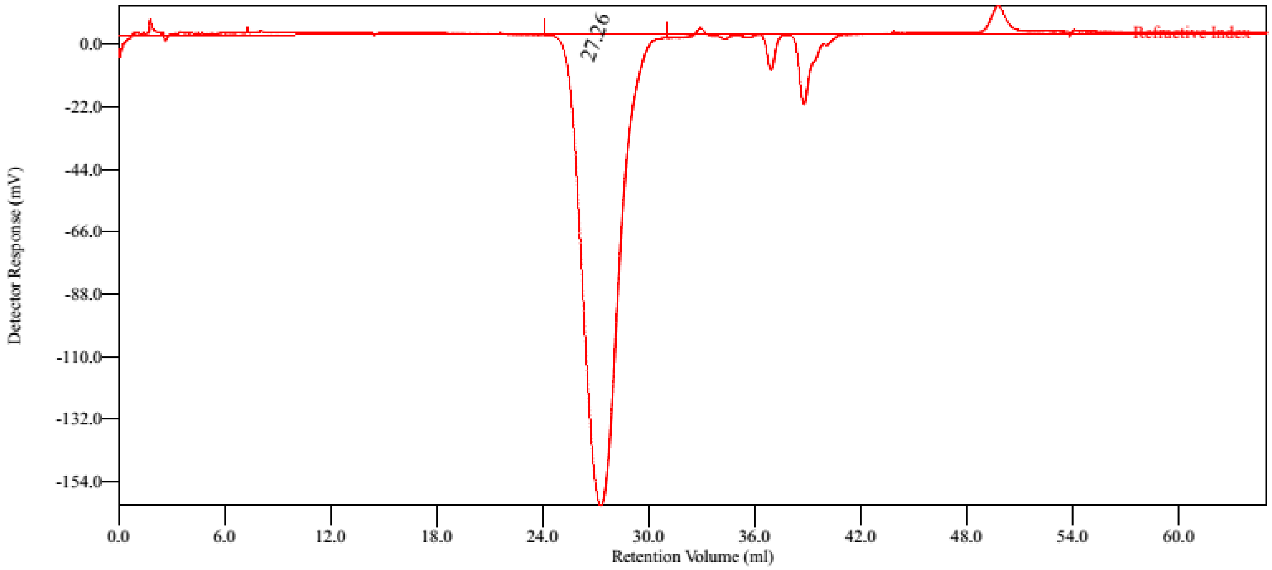
Column Temp. - (deg C)	22.0
OmniSEC Build Number	257

Figure S1. GPC trace of the **P1**-9.6k fraction.



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	27.260
Mn - (Daltons)	13,380
Mw - (Daltons)	20,477
Mz - (Daltons)	28,876
Mp - (Daltons)	17,740
Mw / Mn	1.530
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
Mw 10.0% Low	5,192
Mw 10.0% High	49,415
Wt Fr (Peak)	1.000
RI Area - (mvml)	373.49
UV@510nm Area - (mvml)	0.00

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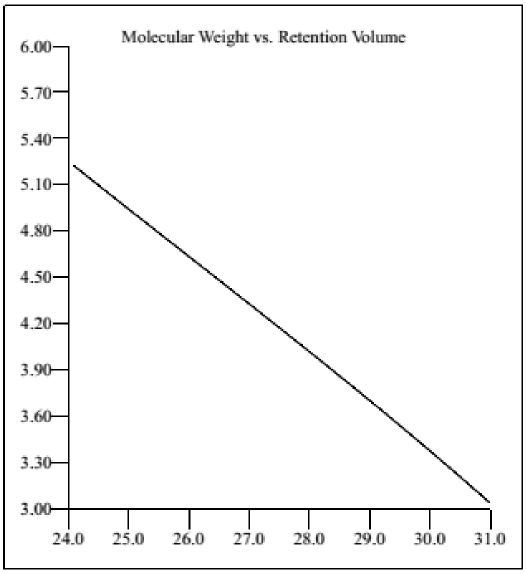
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	120.0
Column Temp. - (deg C)	120.0
OmniSEC Build Number	406



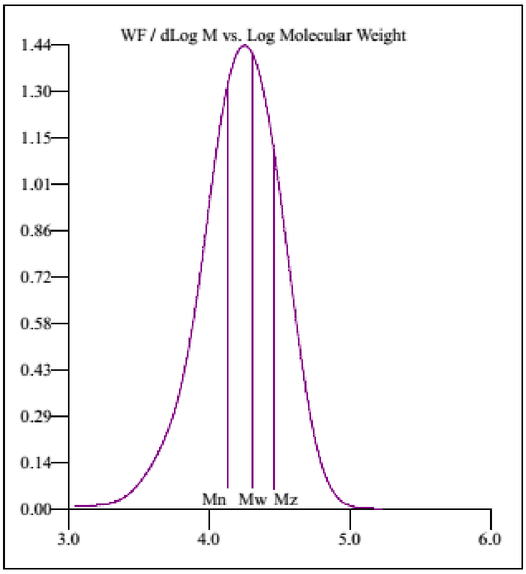
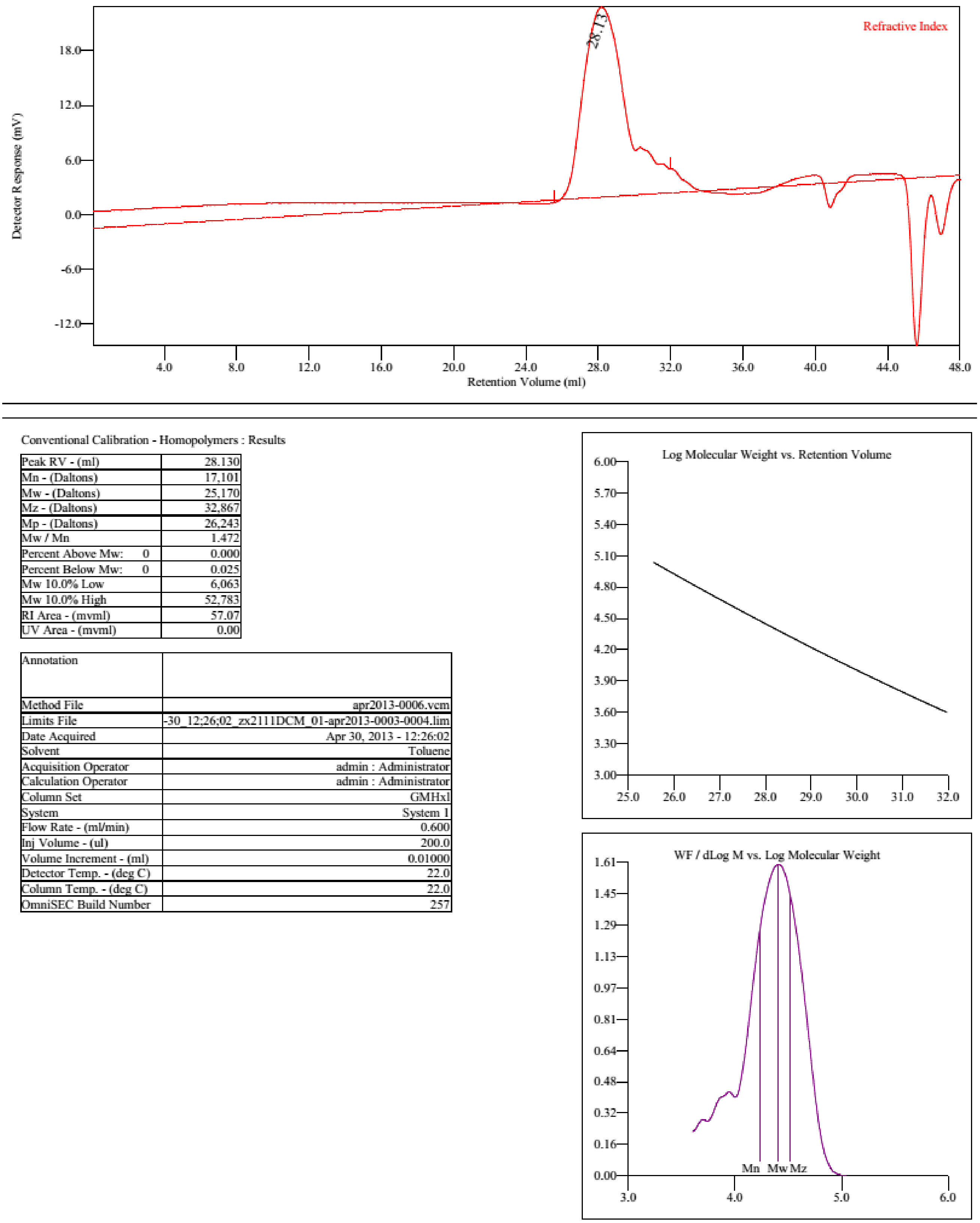


Figure S2. HT-GPC trace of the **P1**-9.6k fraction.



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	28.130
Mn - (Daltons)	17,101
Mw - (Daltons)	25,170
Mz - (Daltons)	32,867
Mp - (Daltons)	26,243
Mw / Mn	1.472
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.025
Mw 10.0% Low	6,063
Mw 10.0% High	52,783
RI Area - (mvml)	57.07
UV Area - (mvml)	0.00

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Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.01000
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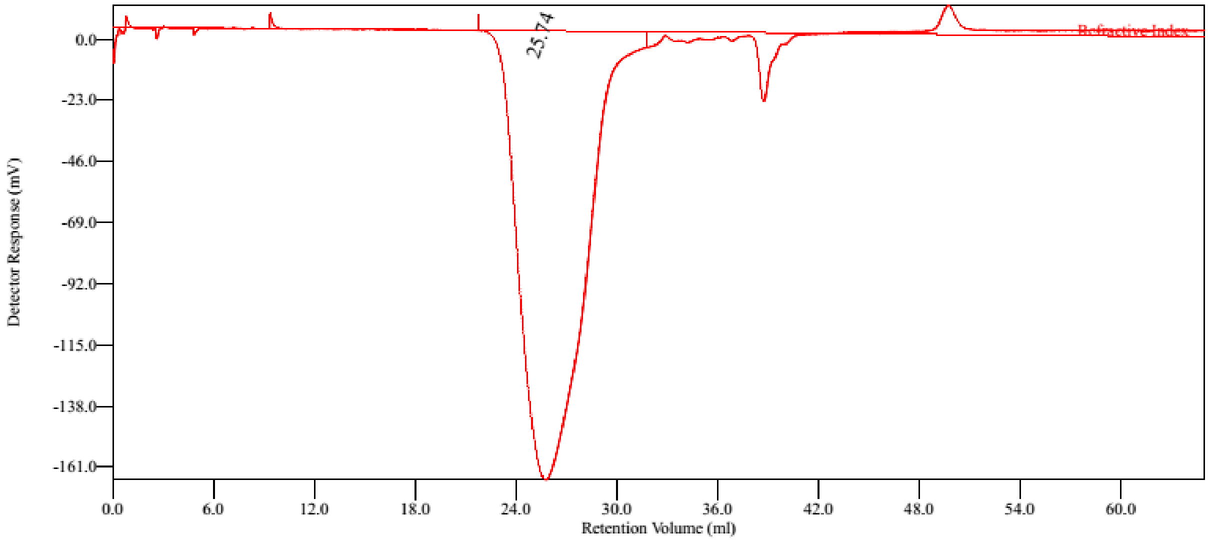
Column Temp. - (deg C)	22.0
OmniSEC Build Number	257

Figure S3. GPC trace of the **P1**-17.1k fraction.



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	25.737
Mn - (Daltons)	15,752
Mw - (Daltons)	59,662
Mz - (Daltons)	128,420
Mp - (Daltons)	52,090
Mw / Mn	3.788
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
Mw 10.0% Low	4,616
Mw 10.0% High	208,482
Wt Fr (Peak)	1.000
RI Area - (mvml)	708.00
UV@510nm Area - (mvml)	0.00

Annotation	
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Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
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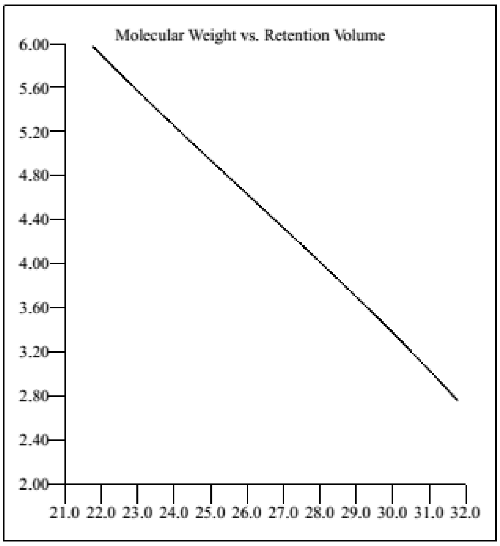
System	HT GPC Malvern
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	120.0
Column Temp. - (deg C)	120.0
OmniSEC Build Number	406



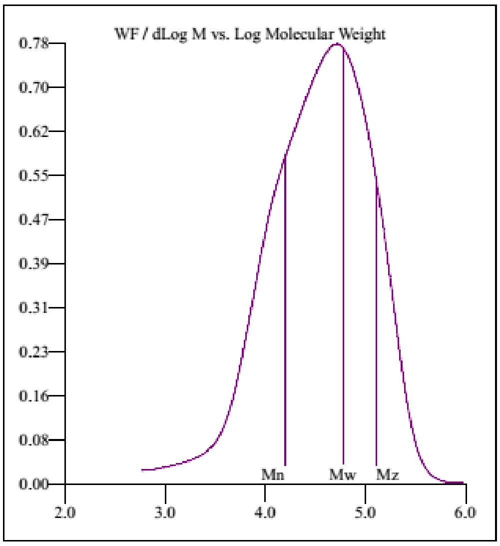
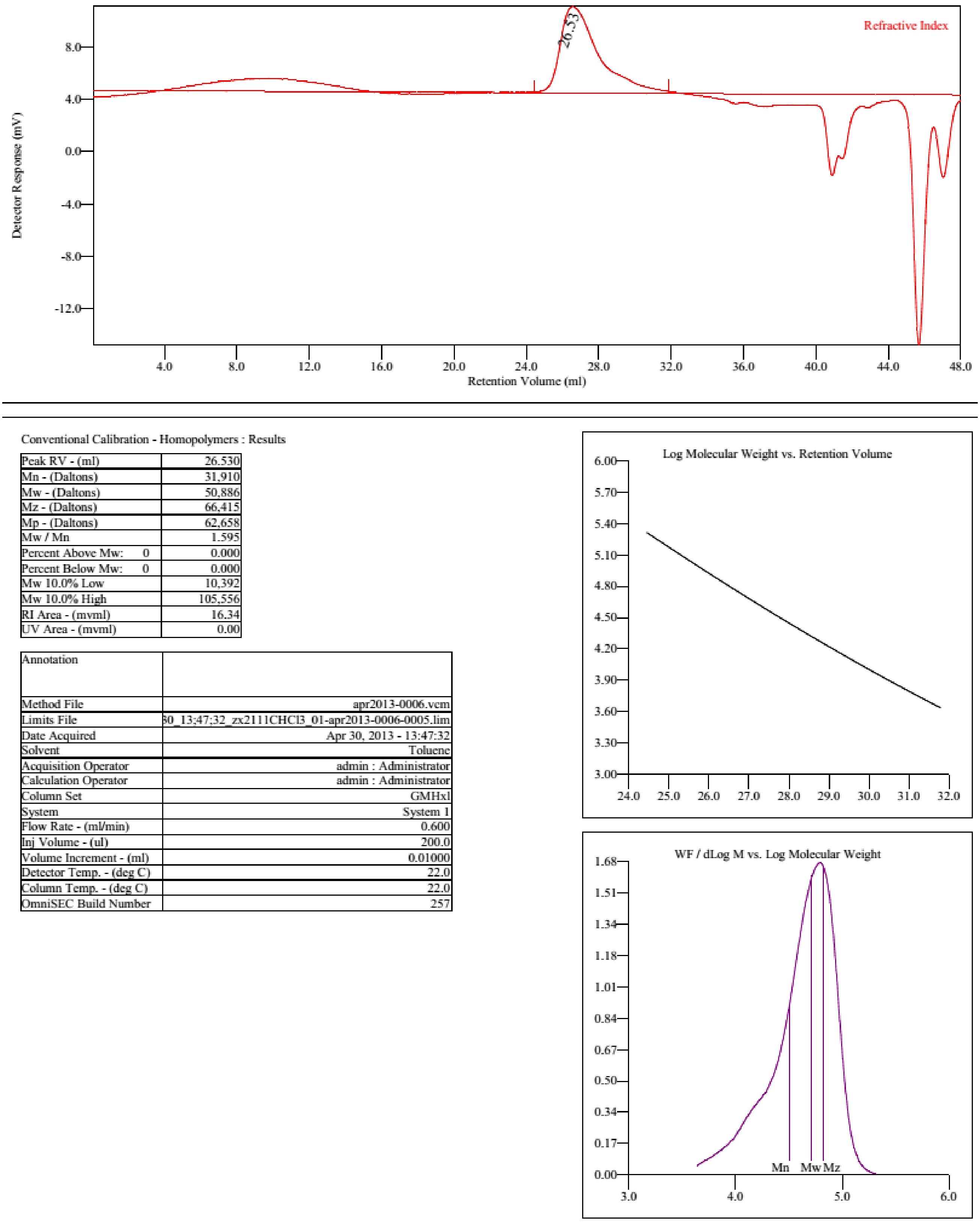


Figure S4. HT-GPC trace of the **P1**-17.1k fraction.



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	26.530
Mn - (Daltons)	31,910
Mw - (Daltons)	50,886
Mz - (Daltons)	66,415
Mp - (Daltons)	62,658
Mw / Mn	1.595
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
Mw 10.0% Low	10,392
Mw 10.0% High	105,556
RI Area - (mvml)	16.34
UV Area - (mvml)	0.00

Annotation	
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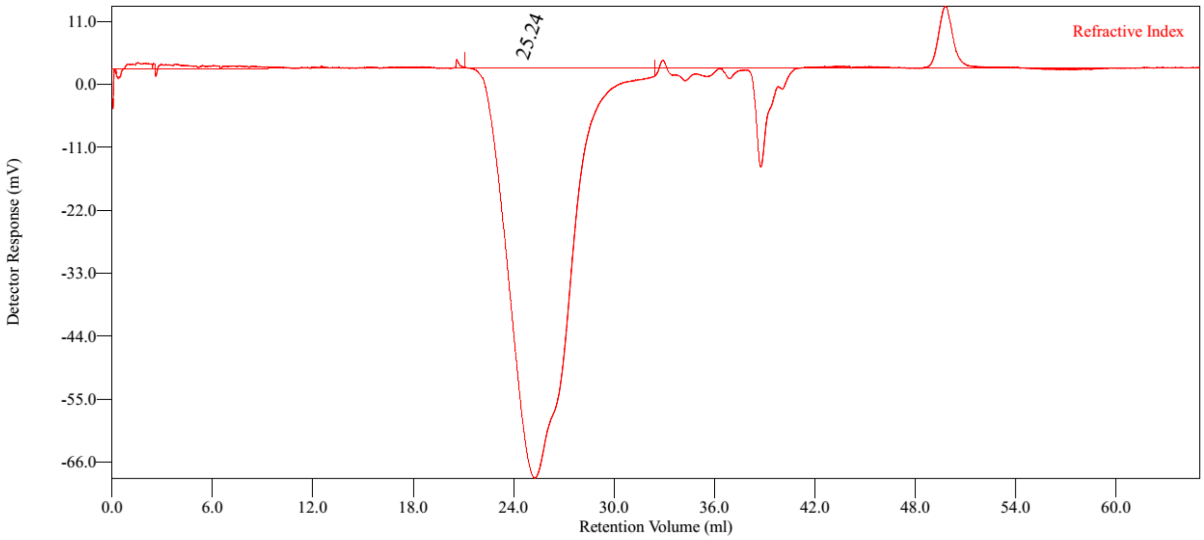
Calculation Operator	admin : Administrator
Column Set	GMHxl
System	System 1
Flow Rate - (ml/min)	0.600
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.01000
Detector Temp. - (deg C)	22.0
Column Temp. - (deg C)	22.0
OmniSEC Build Number	257

Figure S5. GPC trace of the **P1**-32.0k fraction.



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	25.237
Mn - (Daltons)	19,095
Mw - (Daltons)	92,675
Mz - (Daltons)	207,549
Mp - (Daltons)	74,143
Mw / Mn	4.853
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
Mw 10.0% Low	6,883
Mw 10.0% High	334,534
Wt Fr (Peak)	1.000
RI Area - (mvml)	281.39
UV@510nm Area - (mvml)	0.00

Annotation	
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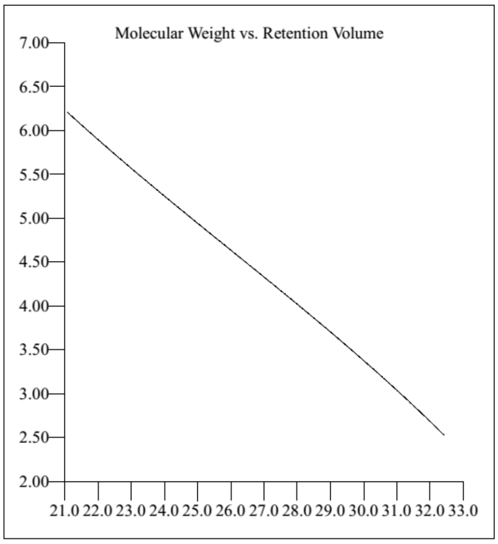
System	HT GPC Malvern
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	120.0
Column Temp. - (deg C)	120.0
OmniSEC Build Number	406



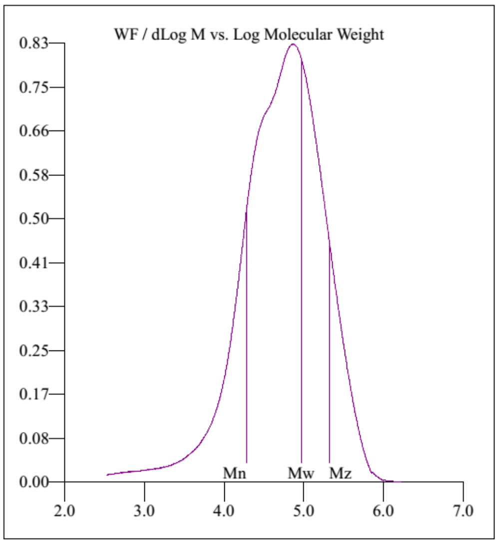
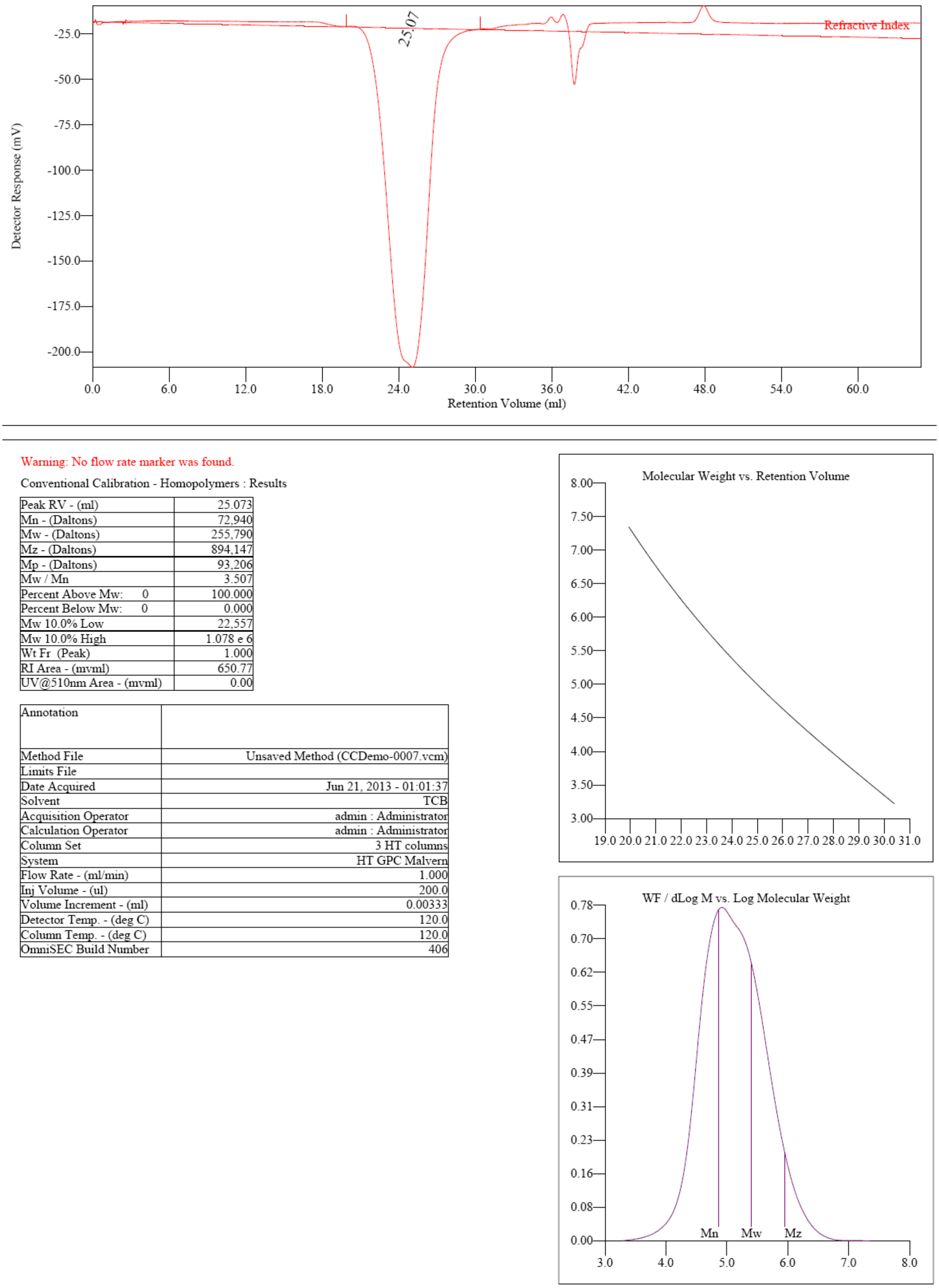


Figure S6. HT-GPC trace of the **P1**-32.0k fraction.



Warning: No flow rate marker was found.

Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	25.073
Mn - (Daltons)	72,940
Mw - (Daltons)	255,790
Mz - (Daltons)	894,147
Mp - (Daltons)	93,206
Mw / Mn	3.507
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
Mw 10.0% Low	22,557
Mw 10.0% High	1.078 e 6
Wt Fr (Peak)	1.000
RI Area - (mvml)	650.77
UV@510nm Area - (mvml)	0.00

Annotation	
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Calculation Operator	admin : Administrator
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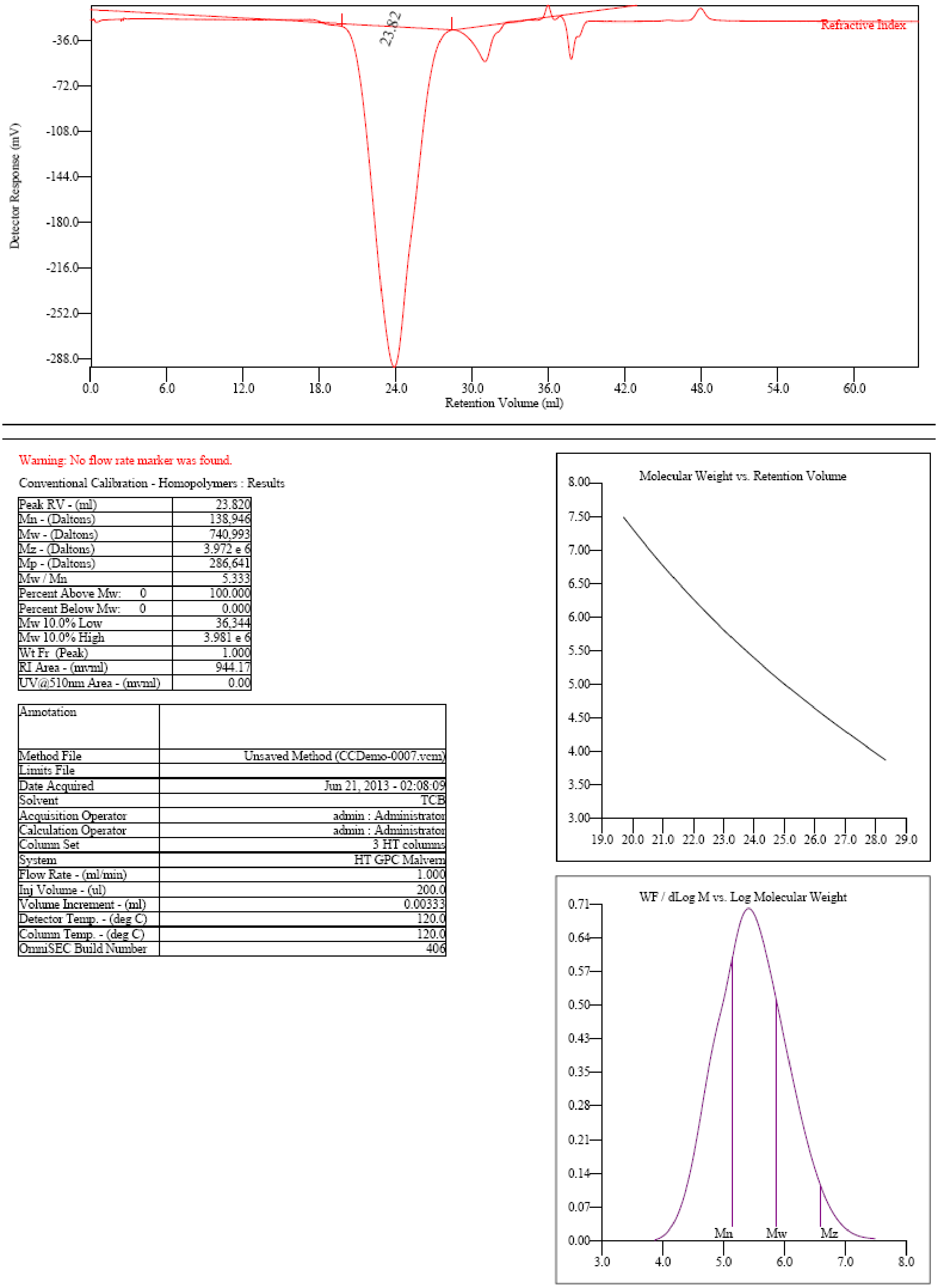
System	HT GPC Malvern
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	120.0
Column Temp. - (deg C)	120.0
OmniSEC Build Number	406

Figure S7. HT-GPC trace of the **P1**-72.9k fraction.



Warning: No flow rate marker was found.

Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	23.820
Mn - (Daltons)	138,946
Mw - (Daltons)	740,993
Mz - (Daltons)	3.972 e 6
Mp - (Daltons)	286,641
Mw / Mn	5.333
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
Mw 10.0% Low	36,344
Mw 10.0% High	3.981 e 6
Wt Fr (Peak)	1.000
RI Area - (mvml)	944.17
UV@510nm Area - (mvml)	0.00

Annotation	
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Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
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OmniSEC Build Number	406

Figure S8. HT-GPC trace of the **P1**-138.9k fraction.

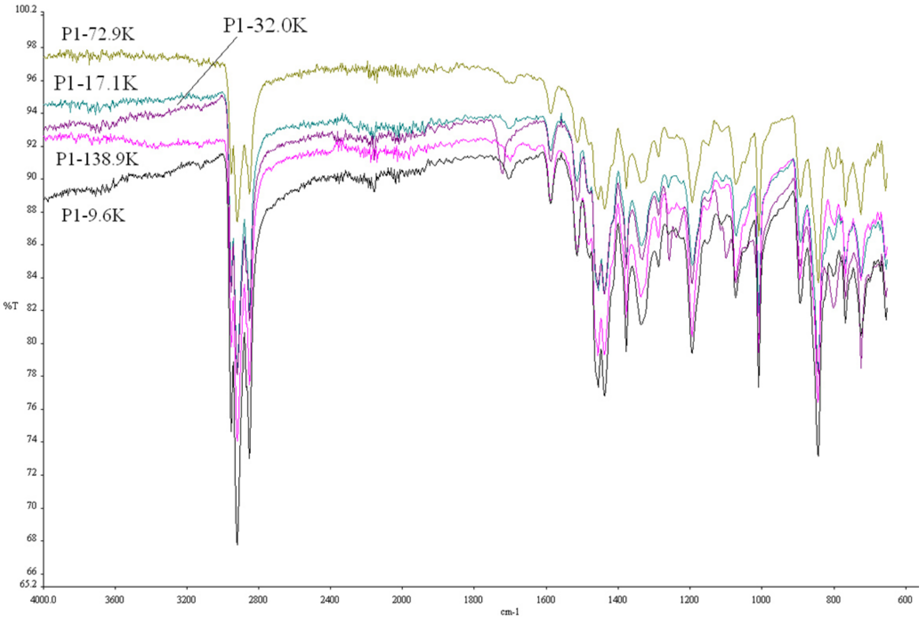


Figure S9. FT-IR spectra of different fractions of polymer **P1**.

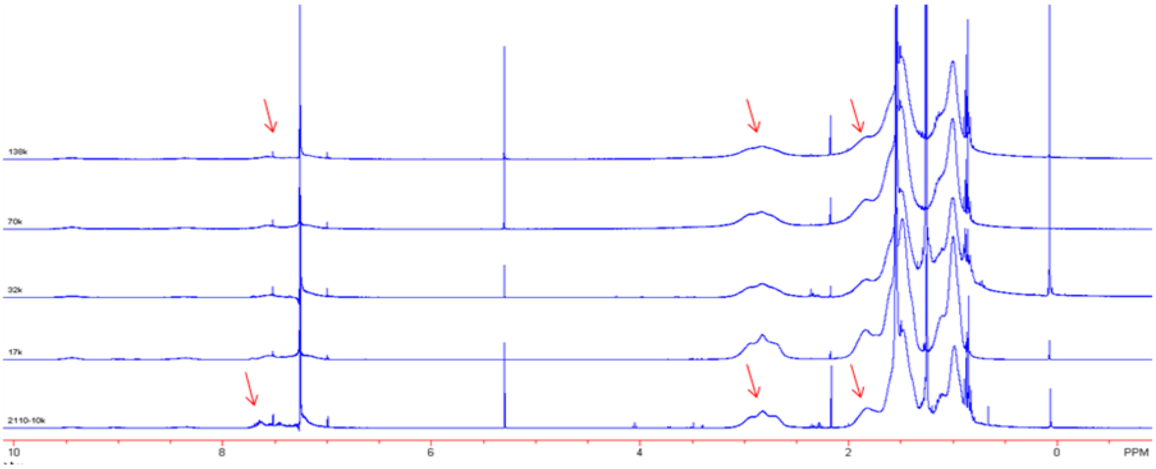


Figure S10. ^{1}H NMR spectra of different fractions of polymer **P1** (10 mg/mL in $CDCl_3$, from bottom to top: **P1**-9.6k, **P1**-17.1k, **P1**-32.0k, **P1**-72.9k, **P1**-138.9k). The red arrows indicate the change of the ^{1}H NMR spectra. Note that the concentration used for the NMR samples was limited by the solubility of the polymers.

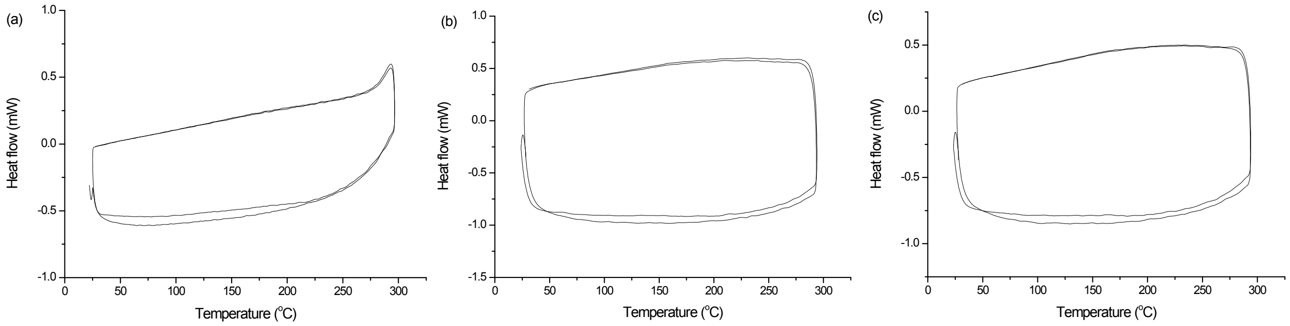


Figure S11. Differential scanning calorimetry (DSC) data for (a) **P1**-17.1k, (b) **P1**-72.9k and (c) **P1**-138k. The DSC data was acquired at a rate of 10 °C per minute and 3 cycles (25 to 300 °C) were recorded. The 2nd and 3rd cycles are shown in this figure.

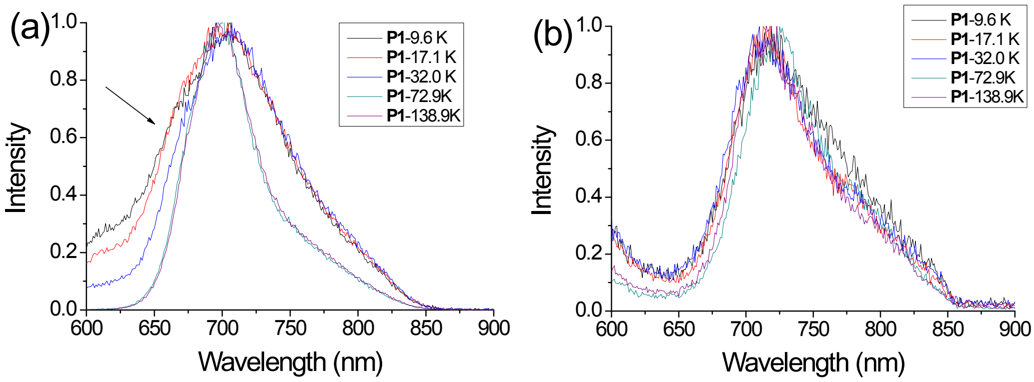


Figure S12. Solution (a) and solid film (b) emission spectra of the polymer fractions (excited at 550 nm). In the solution emission spectra, there is a trend of emission peak narrowing as the MW increase.

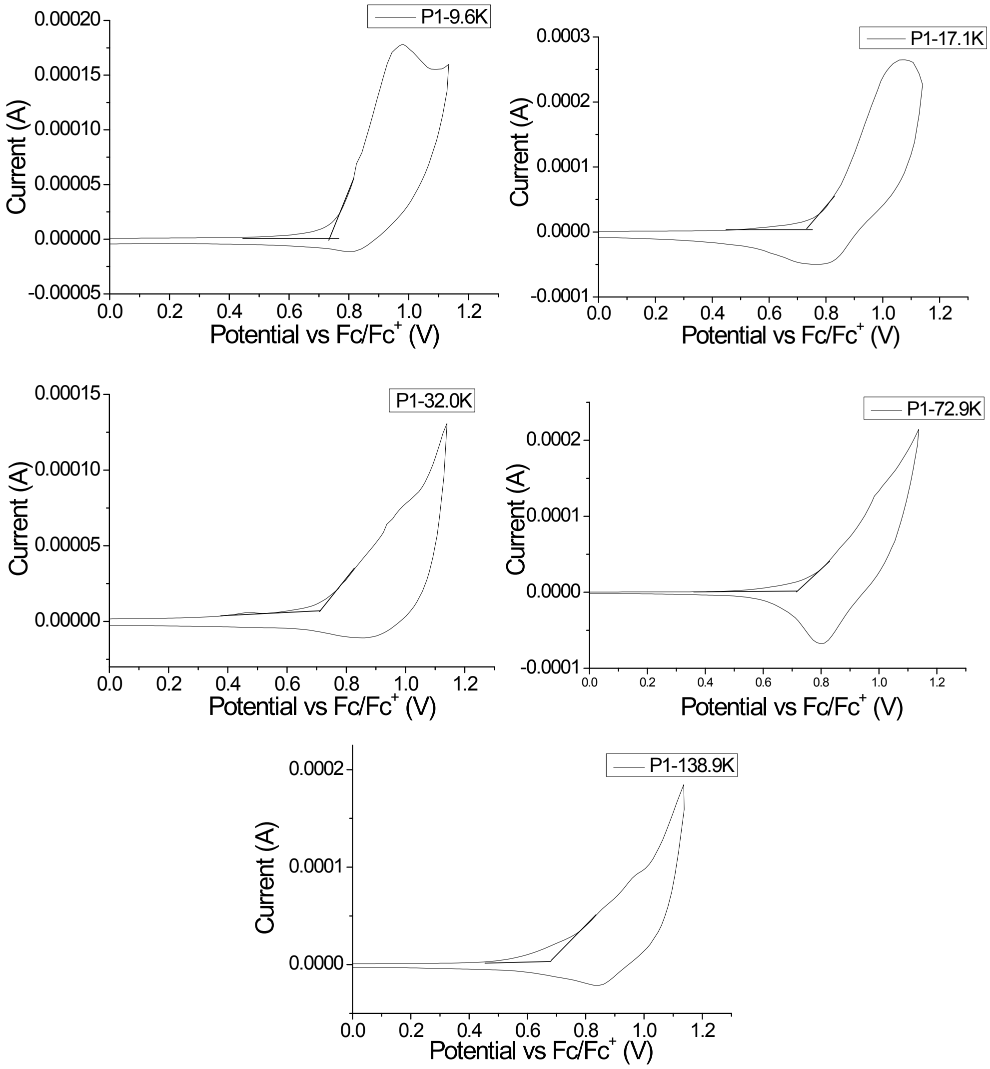


Figure S13. Cyclic voltammograms of the polymer fractions. Ferrocene/ferroceium redox couple was used as the internal standard. The HOMO energy level was calculated from the onset of the oxidation potential of the polymer using the following: $E_{HOMO} = -(4.8 + E_{ox}$ onset) eV.

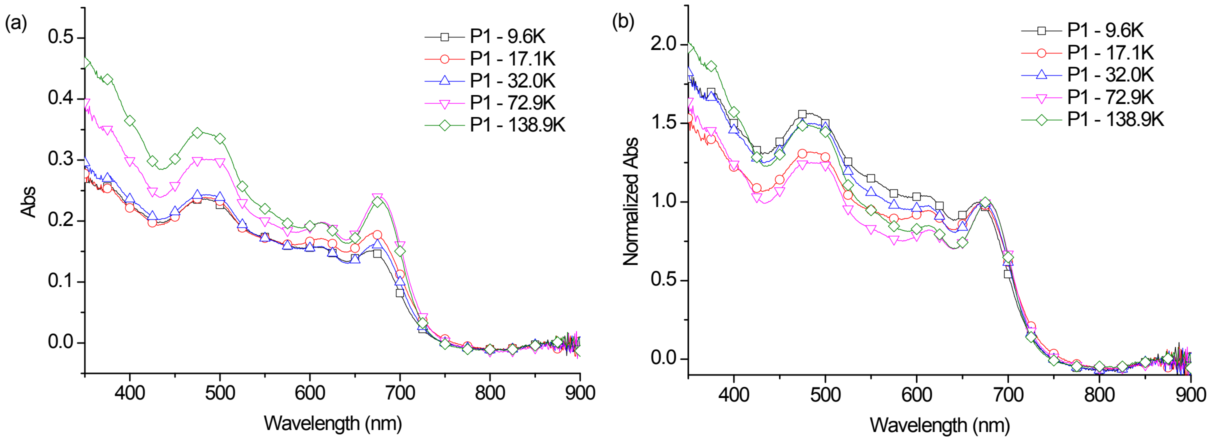
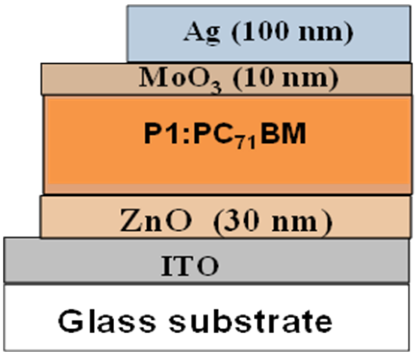


Figure S14. (a) Absorption spectrum from films of polymers **P1** blended with $PC_{71}BM$ in a 1:2 weight ratio and (b) absorption spectra normalized at the λ_{max} of the absorption band at 670 nm.

Fabrication of the BHJ polymer solar cells

Polymer solar cells were processed on pre-patterned indium tin oxide (ITO) coated glass substrates with a sheet resistance of 15 Ω per square. First a thin layer of ZnO nanopaticle (30 nm) was deposited on the ultrasonically cleaned ITO substrates. An active layer of the device was deposited by spin coating an ODCB solution containing 10 mg of polymer and 20 mg of PC$_{71}$BM. The films were then transferred to a metal evaporation chamber and MoO$_3$ (10 nm) and Ag (100 nm) were deposited through a shadow mask (active area was 0.1 cm^2) at approximately 1 x 10^{-6} torr. Film thickness was determined by Veeco Dektak 150+Surface Profiler. The current density-voltage measurements of the devices were carried out using a 1 kW Oriel solar simulator with an AM 1.5G filter as the light source in conjunction with a Keithley 2400 source measurement unit. Solar measurements were carried out under 1000 W/m^2 AM 1.5G illumination conditions. For accurate measurement, the light intensity was calibrated using a reference silicon solar cell (PV measurements Inc.) certified by the National Renewable Energy Laboratory.



Space charge limited current (SCLC) measurement

The space charge limited current in the polymers were studied using hole-only devices to find the charge-transport properties. The hole-only devices, consisting of active layer sandwiched between a PEDOT:PSS coated ITO electrode and Au counter-electrode as the electron-blocking contact, were fabricated as shown in Fig. S8. From the current density as a function of voltage data, the hole mobility in the space-charge limited current region can be estimated using the Mott-Gurney equation $J=9\ (\varepsilon\mu)/8\ x\ (V^2/d^3)$ where ε is the dielectric constant, μ is the charge-carrier mobility, d is the sample thickness.

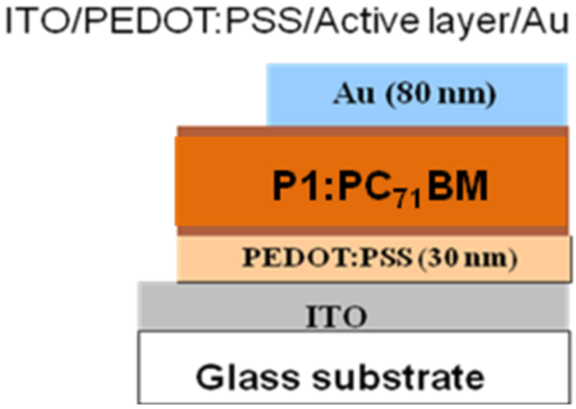


Figure S15. Configuration of the hole only device.