Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Controlling the folding of conjugated polymers at the single molecule level via hydrogen bonding

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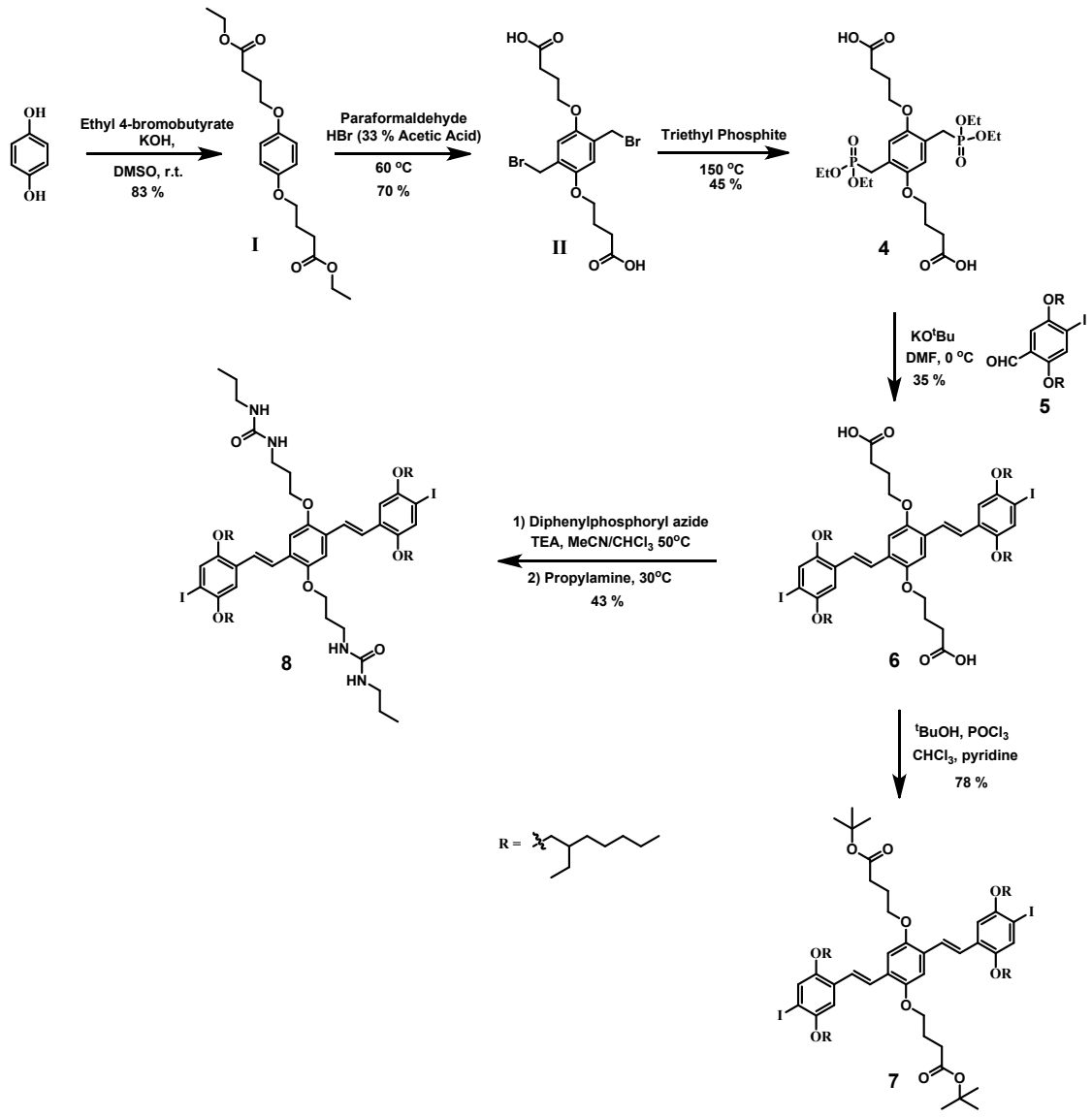
S1. Synthesis



Unless otherwise noted, all reagents were used as received, and all reactions were carried out under an argon atmosphere. Column chromatography was performed on a chromatograph system with normal phase silica columns. ^{1}H NMR and ^{13}C NMR were recorded on a 400 MHz NMR station at room temperature. Synthetic procedures for compounds **5** and **9** can be found in our previous publication.[1]

Diethyl 4,4'-(1,4-phenylenebis(oxy))dibutanoate (I).[2] In a 250 mL round bottom flask was stirred KOH power (7.60 g, 136 mmol) in 150 mL of DMSO at 0 °C under argon. Hydroquinone (3.0 g, 27 mmol) was added followed by ethyl 4-bromobutyrate (14.8 g, 81.6 mmol) slowly. The mixture was stirred at 0 °C for 2 h and stirred at room temperature for 48 h. The mixture was cooled in an ice bath and poured into 1000 mL of cold water. The precipitation was collected under vacuum to give 7.5 g (83.3 %) of a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 4H), 4.14 (q, *J* = 7.1 Hz, 4H), 3.95 (t, *J* = 6.1 Hz, 4H), 2.50 (t, *J* = 7.3 Hz, 4H), 2.12 – 2.04 (m, 4H), 1.25 (dd, *J* = 7.3, 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 153.0, 153.0, 115.4, 77.3, 77.0, 76.7, 67.4, 60.4, 30.8, 24.7, 14.2. Matches previous report.[2]

4,4'-((2,5-bis(bromomethyl)-1,4-phenylene)bis(oxy))dibutanoic acid (II). To a solution of **I** (2.0 g, 5.9 mmol) in 40 mL of AcOH at 60 °C was added paraformaldehyde (0.89 g, 30 mmol) and HBr (6.7 mL, 33% in AcOH). The mixture was stirred overnight at 60 °C and then cooled in an ice bath and poured into 200 mL cold water. The precipitation was filtered and then washed with CH_2Cl_2 to give 1.9 g (70 %) of a white powder. The product was further purified by recrystallization in acetone. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.12 (s, 2H), 7.11 (s, 2H), 4.62 (s, 4H), 4.01 (t, *J* = 6.2 Hz, 4H), 2.45 (t, *J* = 7.3 Hz, 4H), 2.00 – 1.93 (m, 4H).^{13}C NMR (101 MHz, DMSO-d_6) δ 174.6, 150.6, 127.7, 115.3, 67.9, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4, 30.6, 30.2, 24.8. LRMS (ESI) 467.0 HRMS: m/z for $C_{16}H_{19}Br_2O_6$ calc: 464.9548, found 464.9547.

4,4'-((2,5-bis((diethoxyphosphoryl)methyl)-1,4-phenylene)bis(oxy))dibutanoic acid (4). In a 20 mL vial was added **II** (2.0 g, 4.3 mmol) and triethyl phosphite (1.77 g, 10.7 mmol). The mixture was heated at 140 °C for 2 h and then cooled to room temperature. The resulting solid was filtered and was washed with CH_2Cl_2 to give 1.1 g (45 %) of a white solid. The product was further purified by recrystallization in acetone. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.11 (s, 2H), 6.87 (d, *J* = 1.4 Hz, 2H), 3.97 – 3.88 (m, 12H), 3.14 (d, *J* = 20.2 Hz, 4H), 2.42 (t, *J* = 7.3 Hz, 4H), 1.98 – 1.90 (m, 4H), 1.16 (t, *J* = 7.0 Hz, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 174.6, 150.2, 120.0, 115.4, 67.9, 61.7, 40.6, 40.4, 40.2, 40.0, 39.8, 39.5, 39.3, 30.6, 24.9, 16.7, 16.6. LRMS (ESI) 581.2 HRMS: m/z for $C_{24}H_{39}O_{12}P_2$ calc: 581.1917, found 581.1920.

Iodo-Diacid-PPV-Trimer (6). In a 250 mL round bottom flask was stirred **4** (1.20 g, 2.06 mmol) and **5**[1] (3.02 g, 6.18 mmol) in DMF (150 mL) under argon for 10 min at room temperature. t-BuOK (1.16 g, 10.3 mmol) was slowly added and the reaction was vigorously stirred for 4 h at 50 °C. CH_2Cl_2 (300 mL) was added and the mixture was extracted with 1 M HCl (500 mL), water (2 X 500 mL) and brine (100 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue and a catalytic amount of iodine (2.5 mg, 0.01 mmol) was dissolved in toluene (50 mL) and refluxed overnight. The mixture was directly concentrated and purified by silica gel chromatography (0 → 25% EtOAc in hexane, Rf = 0.4) to give 908 mg (35.3 %) of a yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.44, 7.40 (ABq, *J* = 16.6 Hz, 4H), 7.29 (s, 2H), 7.12 (s, 2H), 7.09 (s, 2H), 4.08 (t, *J* = 6.0 Hz, 4H), 3.91 (d, *J* = 5.4 Hz, 4H), 3.87 – 3.80 (m, 4H), 2.59 (t, *J* = 7.1 Hz, 4H), 2.19 – 2.11 (m, 4H), 1.79 – 1.69 (m, 4H), 1.60 – 1.25 (m, 32H), 0.97 – 0.83 (m, 24H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 178.1, 152.3, 151.3, 150.7, 127.8, 127.2, 123.5, 123.1, 110.0, 109.1, 85.3, 72.1, 71.9, 67.8, 53.9, 53.7, 53.4, 53.1, 52.9, 39.6, 30.7, 30.5, 30.4, 29.0, 24.5, 24.1, 24.0, 23.1, 13.9, 13.8, 11.0. LRMS (ESI) 1249.5 HRMS: m/z for $C_{62}H_{91}I_2O_{10}$ calc. 1249.4702, found 1249.4692.

Iodo-Di-^{t}Butyl-PPV-Trimer (7). To a solution of **6** (200 mg, 0.160 mmol) in 10 mL $CHCl_3$, pyridine

(0.25 mL, 3.2 mmol) and t-BuOH (474 mg, 6.40 mmol) was added $POCl_3$ (0.08 mL, 0.9 mmol) dropwise at 0 °C. The mixture was stirred for 5 h at room temperature. CH_2Cl_2 (100 mL) was added and the mixture was extracted with water (2 X 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (0 → 30% CH_2Cl_2 in hexane, Rf = 0.4) to give 124 mg (56.9 %) of a yellow oil. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.49, 7.42 (ABq, *J* = 16.6 Hz, 4H), 7.31 (s, 2H), 7.15 (s, 2H), 7.12 (s, 2H), 4.07 (t, *J* = 6.3 Hz, 4H), 3.95 (d, *J* = 5.4 Hz, 4H), 3.90 – 3.84 (m, 4H), 2.45 (t, *J* = 7.2 Hz, 4H), 2.12 (t, *J* = 6.7 Hz, 4H), 1.83 – 1.73 (m, 4H), 1.63 – 1.28 (m, 32H), 1.40 (s, 18 H), 1.01 – 0.86 (m, 24 H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 172.0, 152.3, 151.4, 150.9, 128.0, 127.3, 123.5, 123.5, 123.1, 110.3, 109.3, 85.2, 80.0, 72.1, 71.9, 68.3, 53.7, 53.4, 53.1, 39.6, 32.0, 30.7, 30.6, 29.1, 27.8, 25.0, 24.1, 24.0, 23.1, 13.9, 13.9, 11.0. LRMS (ESI) 1363.6 HRMS): m/z for $C_{70}H_{108}I_2O_{10}$ calc. 1362.6032, found 1362.5995.

Iodo-Diurea-PPV-Trimer (8). To a solution of **6** (170 mg, 0.14 mmol) in anhydrous MeCN/$CHCl_3$ (10 mL/10 mL) was added Et_3N (0.045 mL, 0.33 mmol) and diphenylphosphoryl azide (0.070 mL, 0.33 mmol). The mixture was stirred for 1 h at room temperature, and then heated for another 2 h at 50 °C. The reaction mixture was cooled to room temperature, and propylamine (0.1 mL, 1.36 mmol) was added. The mixture was stirred at 30 °C overnight and then directly concentrated and purified by silica gel chromatography (0 → 35% EtOAc in hexane, Rf = 0.4) to give 80 mg (43.2 %) of a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44, 7.38 (ABq, *J* = 16.4 Hz, 4H), 7.30 (s, 4H), 7.09 (s, 4H), 7.01 (s, 4H), 4.65 (t, *J* = 5.6 Hz, 4H), 4.14 (t, *J* = 5.6 Hz, 4H), 4.07 (t, *J* = 5.7 Hz, 2H), 3.91 (d, *J* = 5.4 Hz, 4H), 3.88 – 3.81 (m, 4H), 3.43 (dd, *J* = 12.0, 5.9 Hz, 4H), 2.92 (dd, *J* = 13.7, 6.4 Hz, 4H), 2.10 – 2.01 (m, 4H), 1.81-1.72 (m, 4H), 1.60 – 1.24 (m, 36H), 0.99 – 0.85 (m, 24H), 0.78 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 157.9, 152.4, 151.3, 150.7, 127.6, 127.2, 123.9, 123.6, 110.4, 109.3, 85.5, 72.1, 72.0, 67.3, 53.9, 53.7, 53.4, 53.1, 52.9, 42.1, 39.6, 39.5, 38.0, 30.6, 30.5, 29.9, 29.1, 29.0, 24.1, 23.9, 23.4, 23.0, 13.9, 13.8, 11.2, 11.01, 10.97. LRMS (ESI) 1363.6 HRMS: m/z for $C_{68}H_{109}I_2N_4O_8$ calc. 1363.6335, found 1363.6282.

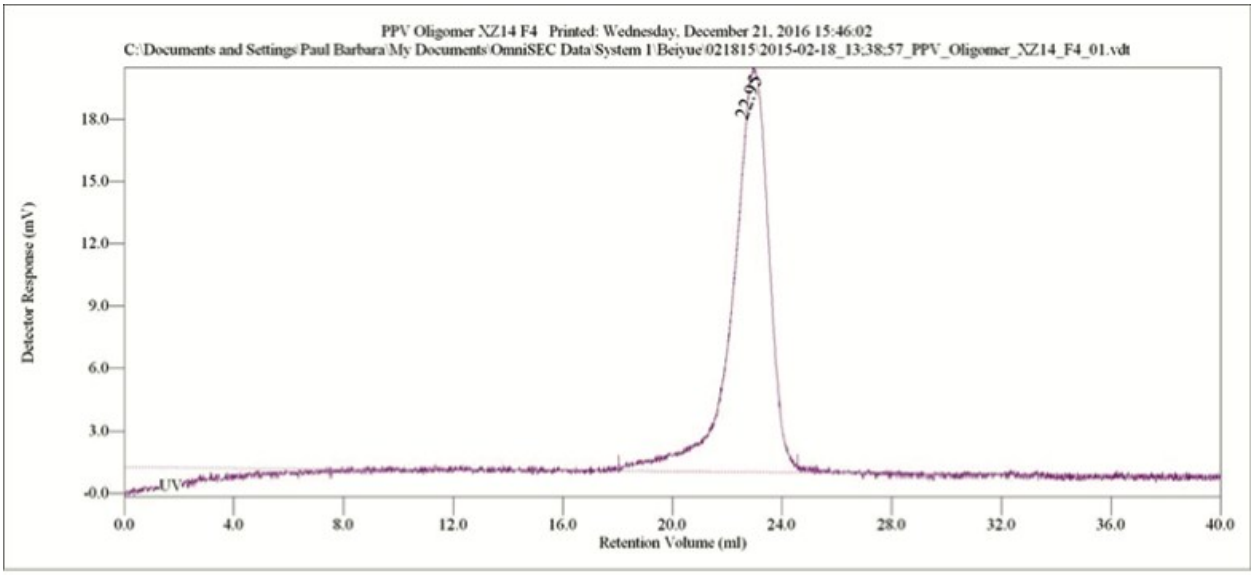
Di-t-butyl trimer-co-alkoxy-polymer (1). In a glovebox were combined **7** (92.1 mg, 0.0676 mmol), **9**[1] (27.5 mg, 0.0696 mmol), $Pd(PPh_3)_4$ (3.9 mg, 0.0034 mmol), CuI (0.65 mg, 0.0034 mmol), toluene (10 mL) and diisopropylamine (2 mL) in a sealed tube. The reaction vessel was sealed and heated at 85 °C for 3 days. The reaction mixture was filtered and the filtrate was concentrated. The residue was repetitively precipitated from THF by dropwise addition to methanol, hexane, and then methanol to give a brown tacky product (54 mg, 53.5 %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.52 (s, 4H), 7.47 (d, *J* = 8.6 Hz, 4H), 7.21 (d, *J* = 14.4 Hz, 4H), 7.03 (s, 2H), 6.93 (d, *J* = 8.7 Hz, 4H), 4.18-4.14 (m, 4H), 4.10 (t, *J* = 6.1 Hz, 4H), 4.05-4.00 (m, 4H), 3.97 – 3.90 (m, 4H), 3.87-3.83 (m, 4H), 3.73-3.64 (m, 8H), 2.48 (t, *J* = 7.2 Hz, 4H), 2.19 – 2.11 (m, 4H), 1.87-1.78 (m, 4H), 1.67-1.30 (m, 32H), 1.42 (s, 18H), 1.03-0.88 (m, 24H). Mn = 40,053, PDI = 1.3.

Di-carboxylic acid trimer-co-alkoxy-polymer (2). In a glovebox were combined **6** (54.5 mg, 0.0436 mmol), **9**[1] (17.5 mg, 0.0449 mmol), $Pd(PPh_3)_4$ (2.5 mg, 0.00218 mmol), CuI (0.42 mg, 0.00218 mmol), THF (5 mL), water (1 mL) and diisopropylamine (1.5 mL) in a sealed tube. The reaction vessel was sealed and heated at 65 °C for 3 days. The reaction mixture was filtered and the filtrate was concentrated. The residue was repetitively precipitated from THF by dropwise addition to methanol, hexane, and then methanol to give a brown tacky product (32.1 mg, 48.6 %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.57-7.39 (m, 8H), 7.26-7.11 (s, 4H), 7.04 – 6.98 (m, 2H), 6.97-6.85 (m, 4H), 4.19-4.06 (m, 8H), 4.03-3.78 (m, 12H), 3.73-3.60 (m, 8H), 2.71 – 2.42 (m, 4H), 2.26-2.04 (m, 4H), 1.84 – 1.16 (m, 32H), 1.02 – 0.78 (m, 24H). Mn = 13,140, PDI = 1.6.

Di-urea-trimer-co-alkoxy-polymer (3). In a glovebox were combined **8** (19.47 mg, 0.0143 mmol), **9**[1] (27.4 mg, 0.0694 mmol), $Pd(PPh_3)_4$ (0.83 mg, 0.0007 mmol), CuI (0.13 mg, 0.0007 mmol), THF (5 mL),

water (1 mL) and diisopropylamine (1.5 mL) in a sealed tube. The reaction vessel was sealed and heated at 65 ^{o}C for 3 days. The reaction mixture was filtered and the filtrate was concentrated. The residue was repetitively precipitated from THF by dropwise addition to methanol, hexane, and then methanol to give a brown tacky product (13 mg, 52.0 %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.51 (s, 4H), 7.49 – 7.42 (m, 4H), 7.22 – 7.11 (m, 4H), 7.06 – 6.99 (m, 2H), 6.95 – 6.86 (m, 4H), 4.19-4.09 (m, 8H), 4.01 – 3.80 (m, 12H), 3.72-3.62 (m, 8H), 3.44 – 3.35 (m, 4H), 2.99 – 2.91 (m, 4H), 2.08 – 2.00 (m, 4H), 1.84 – 1.75 (m, 4H), 1.39-1.24 (m, 36H), 1.02-0.77 (m, 30H). Mn = 12,690, PDI = 1.5.

GPC trace of fractionated Polymer **1**



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	22.950
Mn - (Daltons)	12,976
Mw - (Daltons)	19,048
Mz - (Daltons)	54,447
Mp - (Daltons)	11,978
Mw / Mn	1.468
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
Mw 10.0% Low	7,654
Mw 10.0% High	72,031
RI Area - (mvml)	0.00
UV@450nm Area - (mvml)	29.92

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Calculation Operator	autologin : UT Austin NST
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System	System 1
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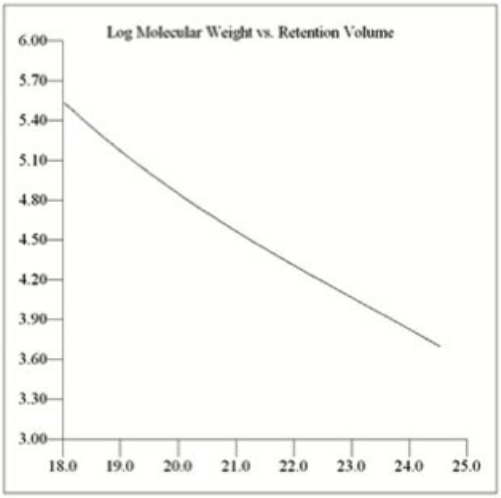
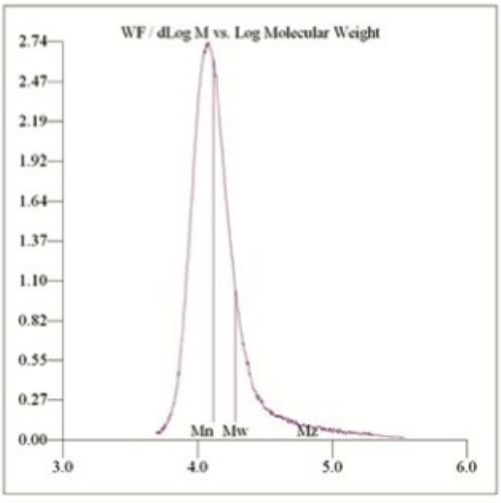
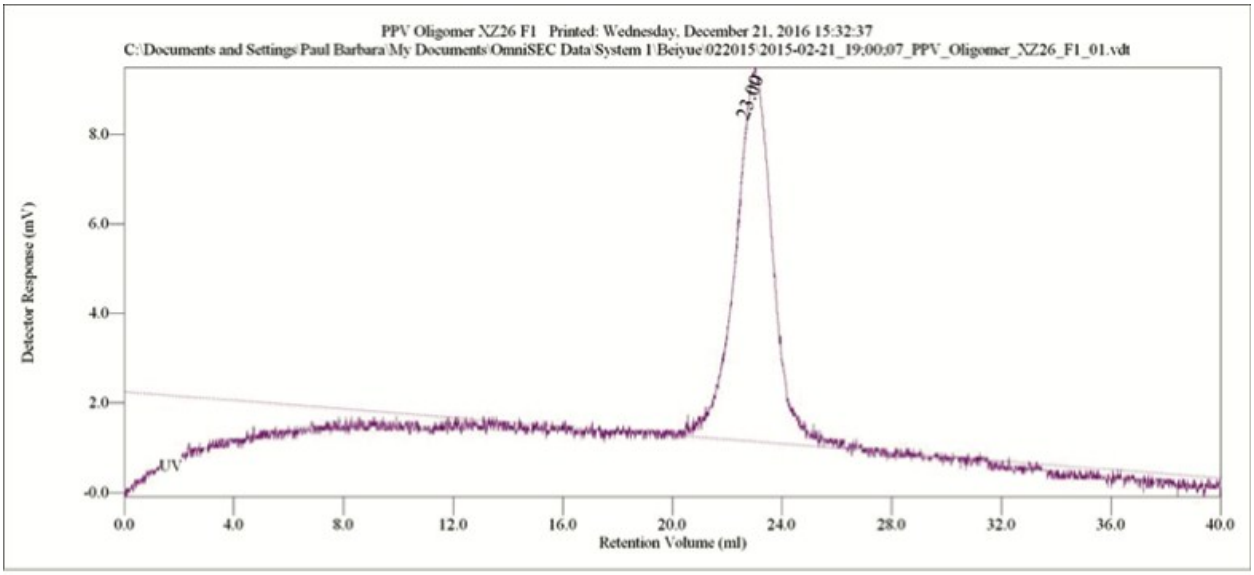
Detector Temp. - (deg C)	35.0
Column Temp. - (deg C)	40.0
OmniSEC Build Number	354





GPC trace of fractionated Polymer **2**



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	22.997
Mn - (Daltons)	11,263
Mw - (Daltons)	13,157
Mz - (Daltons)	15,654
Mp - (Daltons)	11,661
Mw / Mn	1.168
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.006
Mw 10.0% Low	6,251
Mw 10.0% High	25,960
RI Area - (mvml)	0.00
UV@450nm Area - (mvml)	12.89

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Calculation Operator	autologin : UT Austin NST
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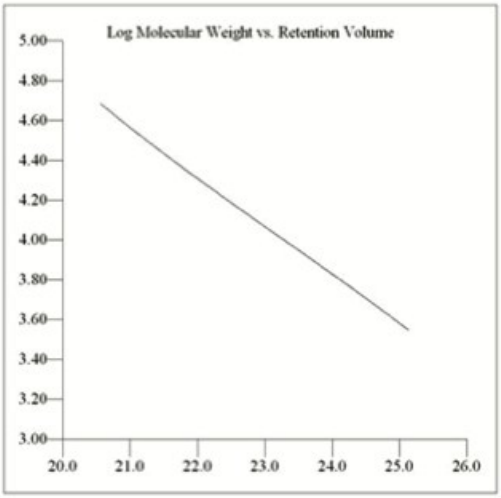
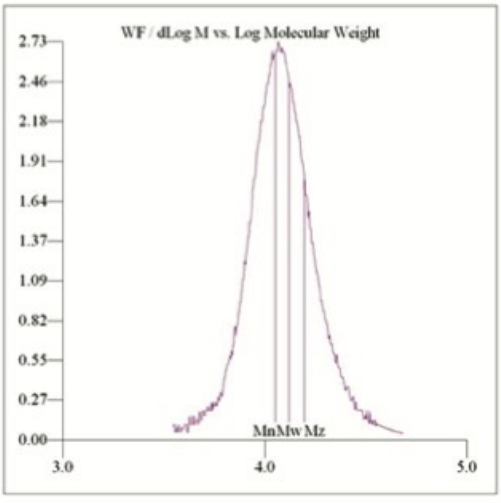
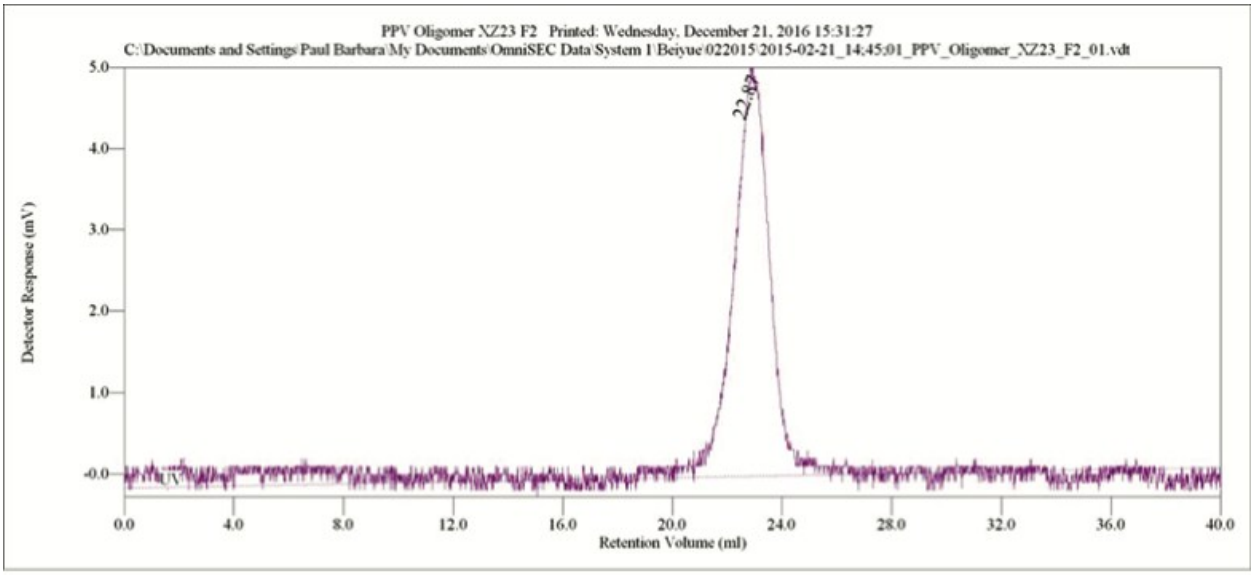
Inj Volume - (ul)	100.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	35.0
Column Temp. - (deg C)	40.0
OmniSEC Build Number	354





GPC trace of fractionated Polymer **3**



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	22.867
Mn - (Daltons)	11,851
Mw - (Daltons)	13,483
Mz - (Daltons)	15,469
Mp - (Daltons)	12,544
Mw / Mn	1.138
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
Mw 10.0% Low	6,888
Mw 10.0% High	25,570
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System	System 1
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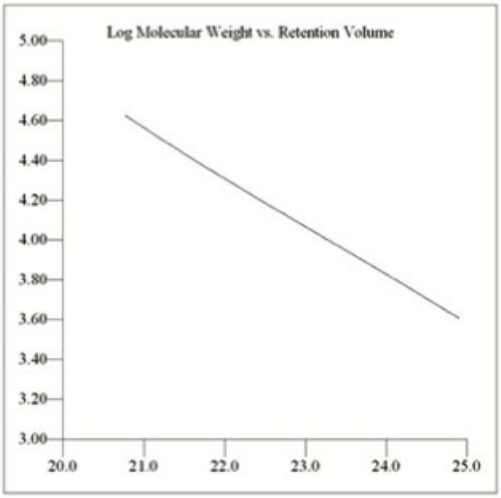
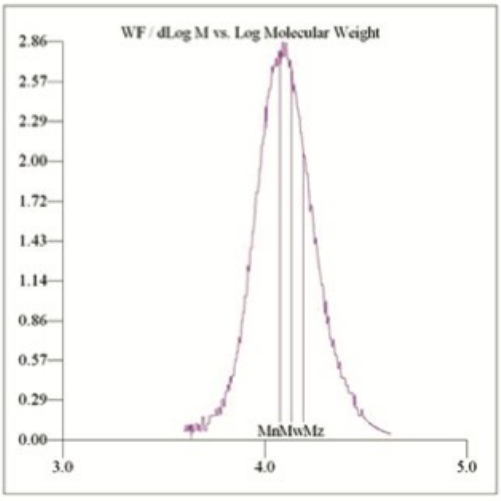
Column Temp. - (deg C)	40.0
OmniSEC Build Number	354





S2. Absorption and Fluorescence Spectra in Other Solvent Systems

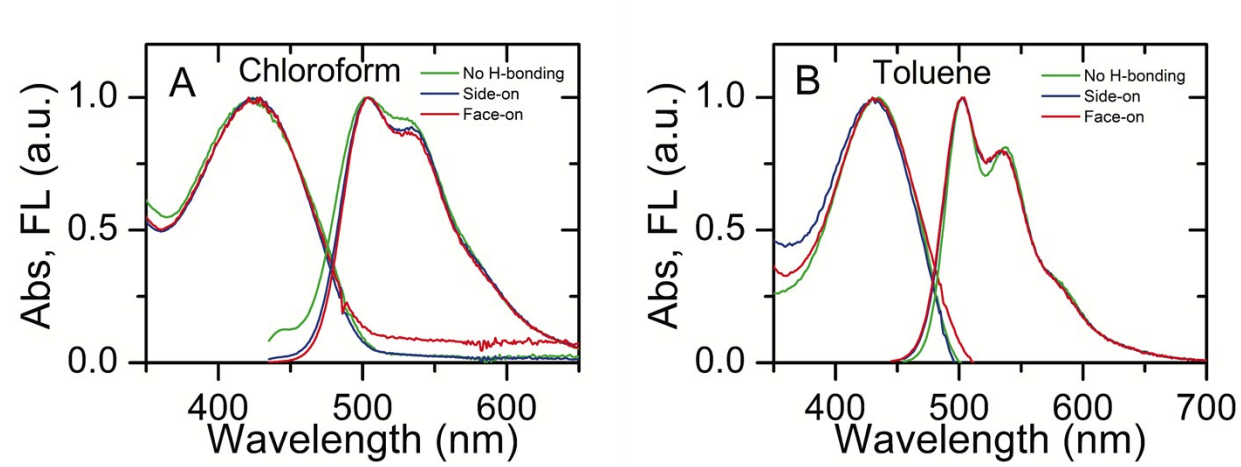


Figure 1S. Absorption and fluorescence emission spectra of all three polymers in A) chloroform and B) toluene.

S3. Single Molecule Spectral Fittings

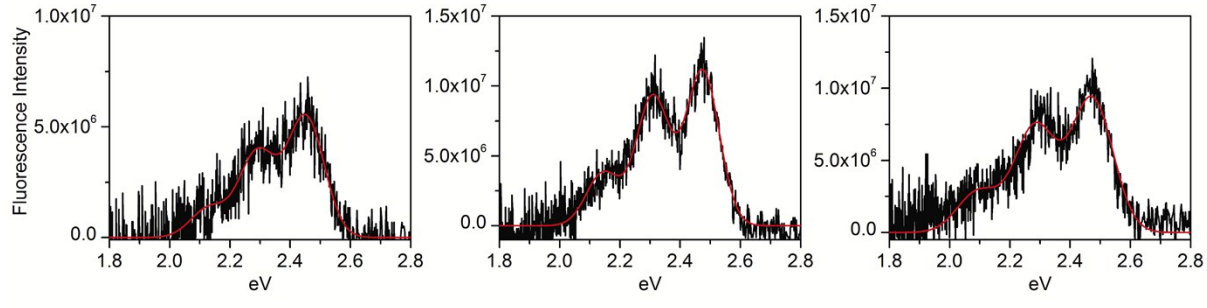


Figure 2S. Sample single molecule spectra (black) with fitting results (red) of polymer **1**.

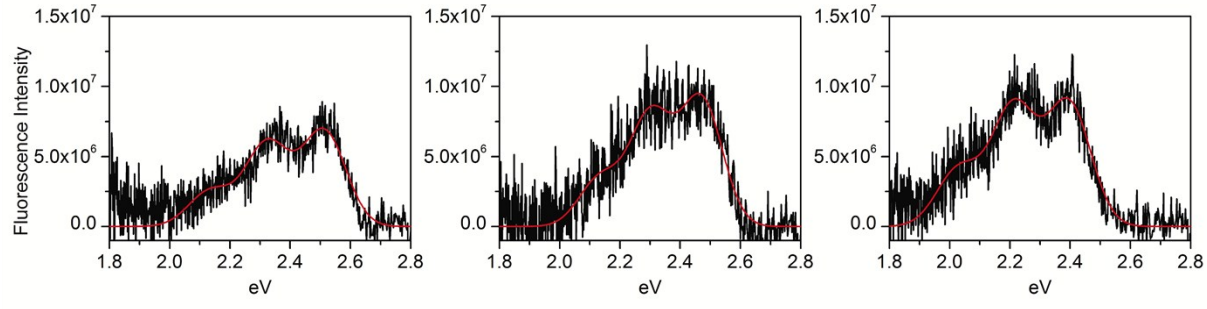


Figure 3S. Sample single molecule spectra (black) with fitting results (red) of polymer **2**.

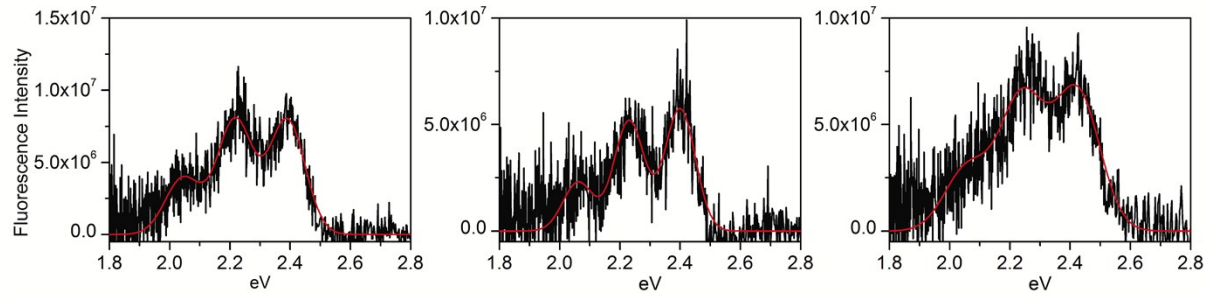


Figure 4S. Sample single molecule spectra (black) with fitting results (red) of polymer **3**.

Polymer	*S Factor*	*E $_{0\text{-}0}$ (eV)*
	Single Molecule	
1 **(no H-Bonding)**	1.04±0.10	2.47±0.03
2 **(Side-on)**	1.06±0.07	2.47±0.03
3 **(Face-on)**	1.11±0.13	2.41±0.02
	Solution	
1 **(no H-Bonding)**	1.096	2.482
2 **(Side-on)**	1.097	2.483
3 **(Face-on)**	1.102	2.474

Table 1S. Franck-Condon fitting results of single molecule and solution fluorescence spectra of all three polymers.

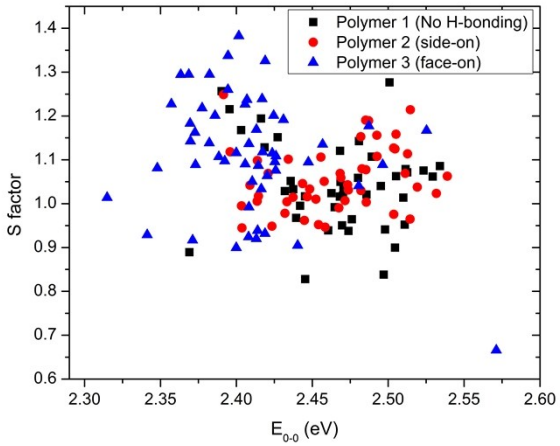
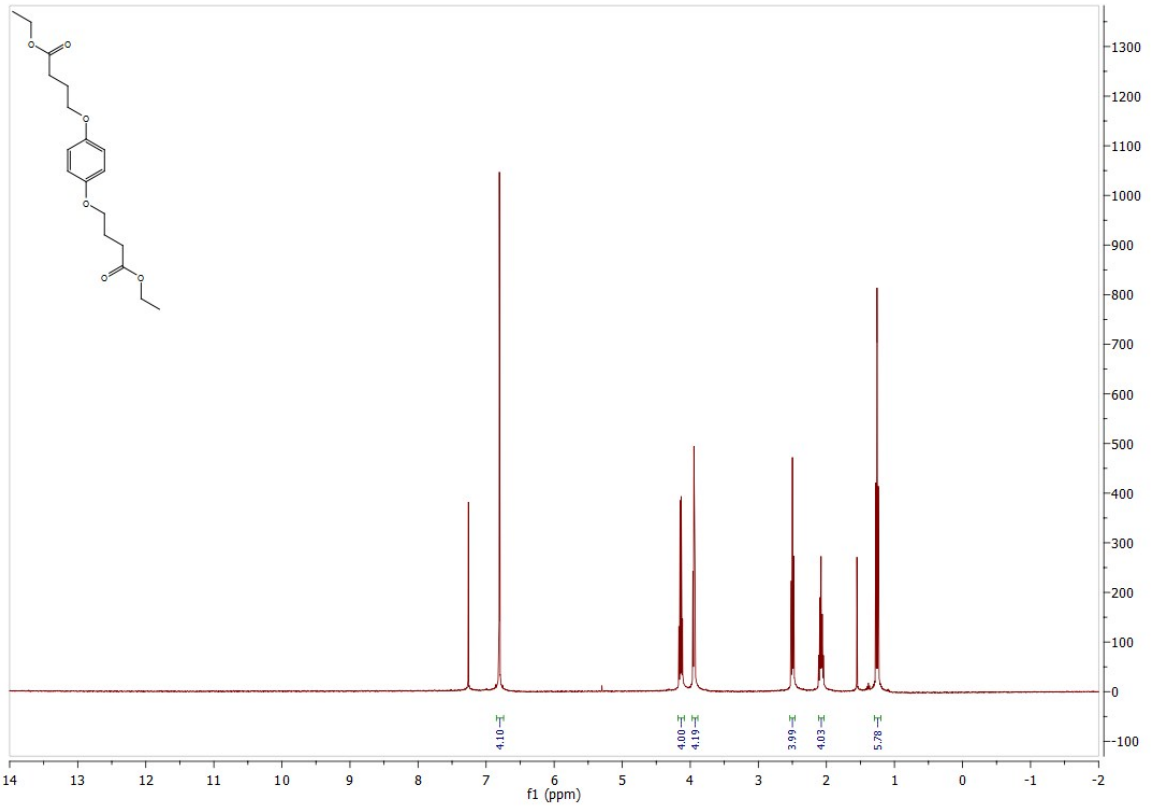
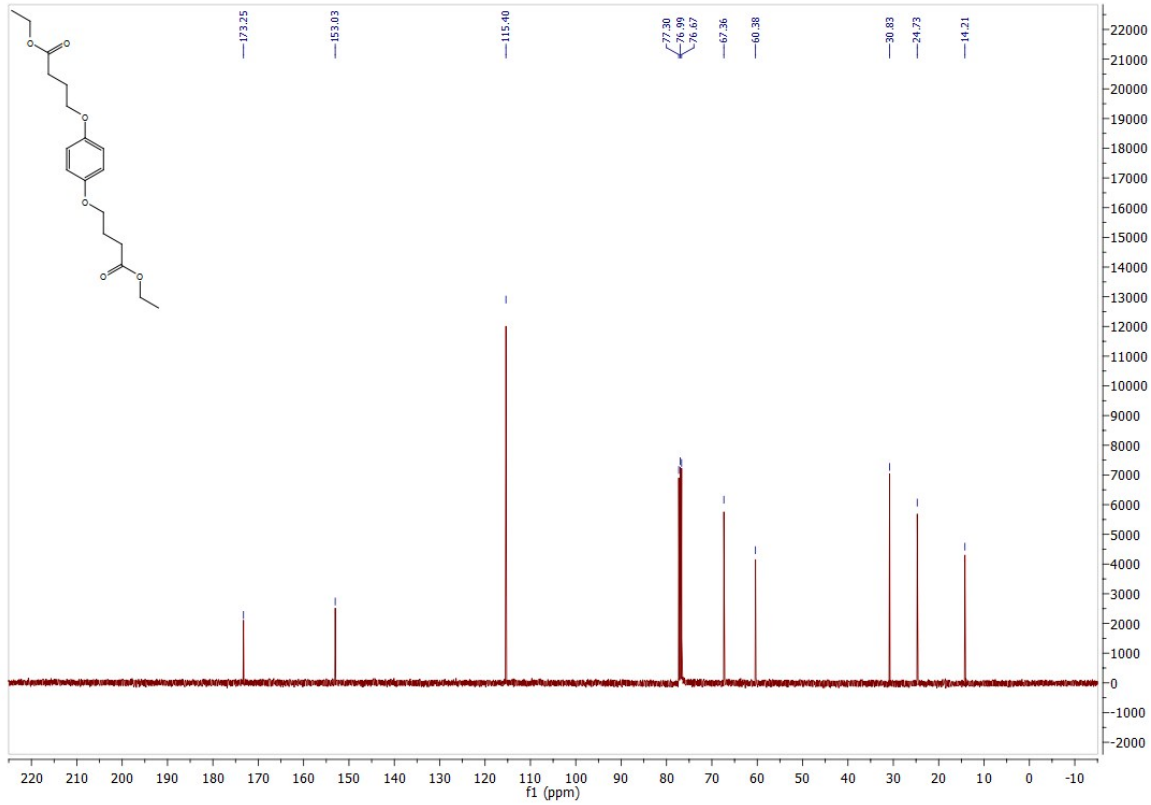


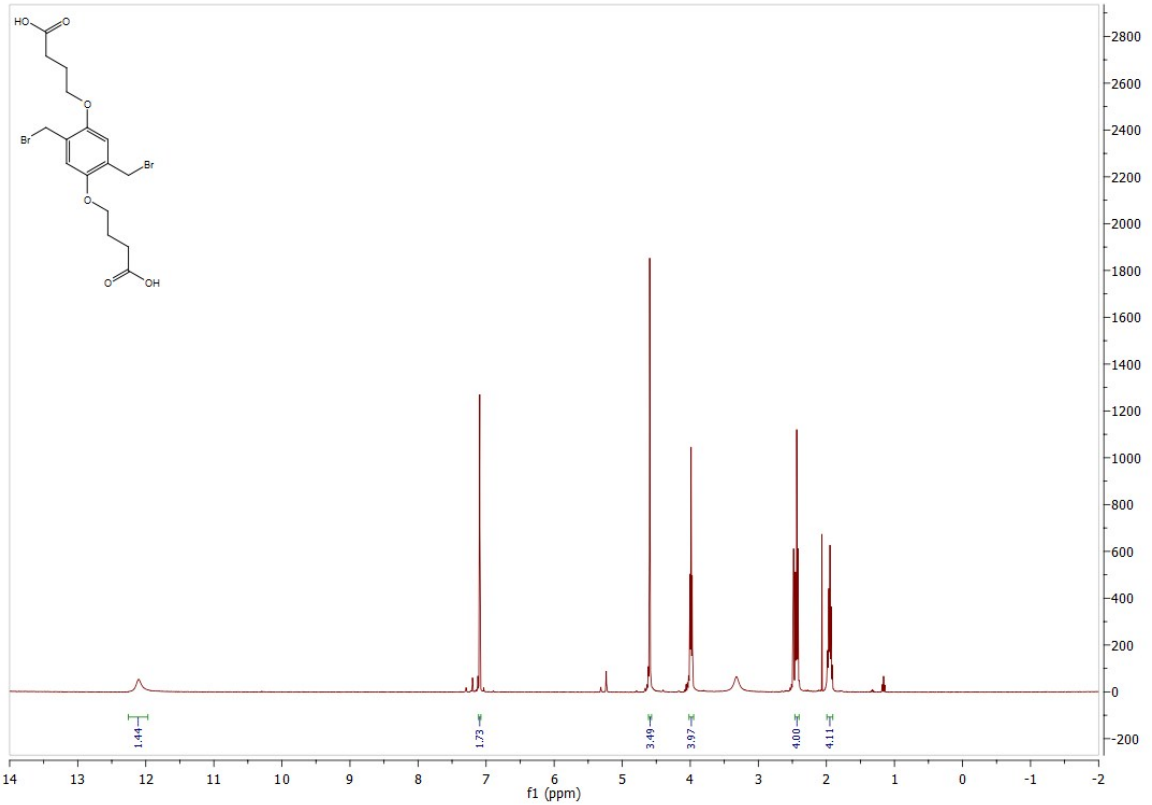
Figure 5S. Scatter plot of S factor vs $E_{0\text{-}0}$ for all the polymers.

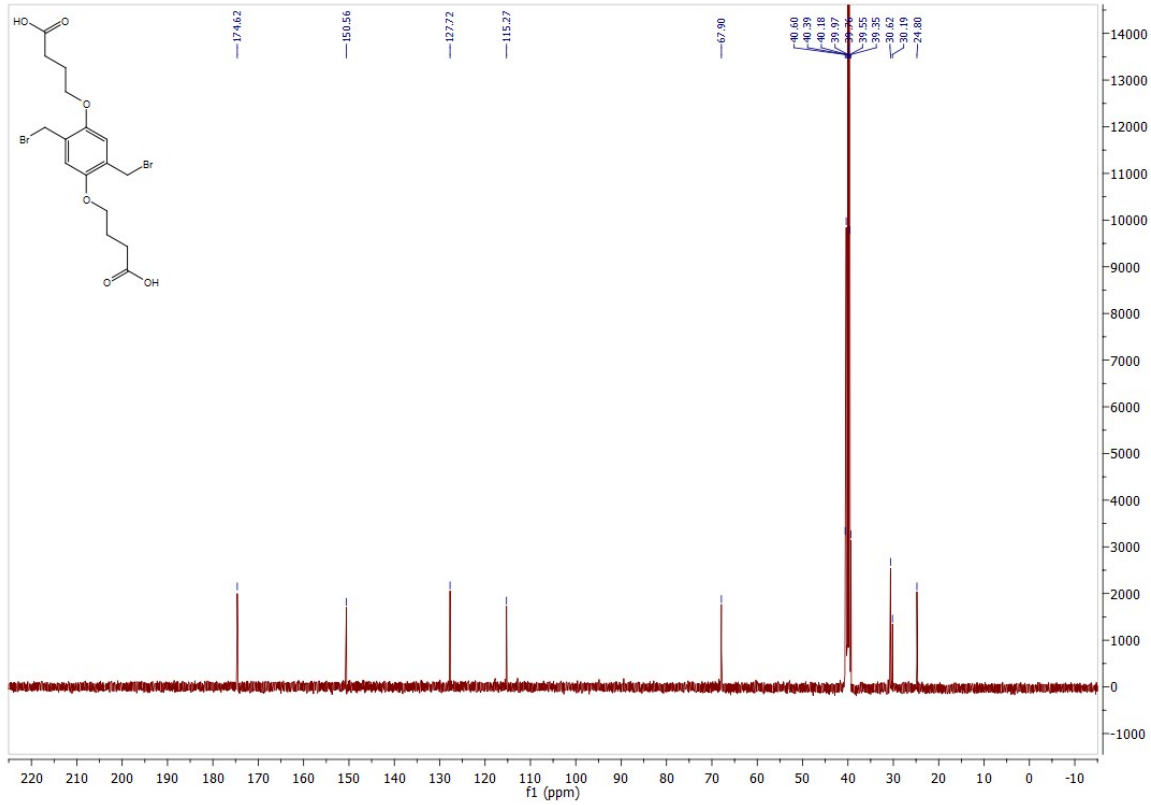
3. NMR Spectra **Compound I**



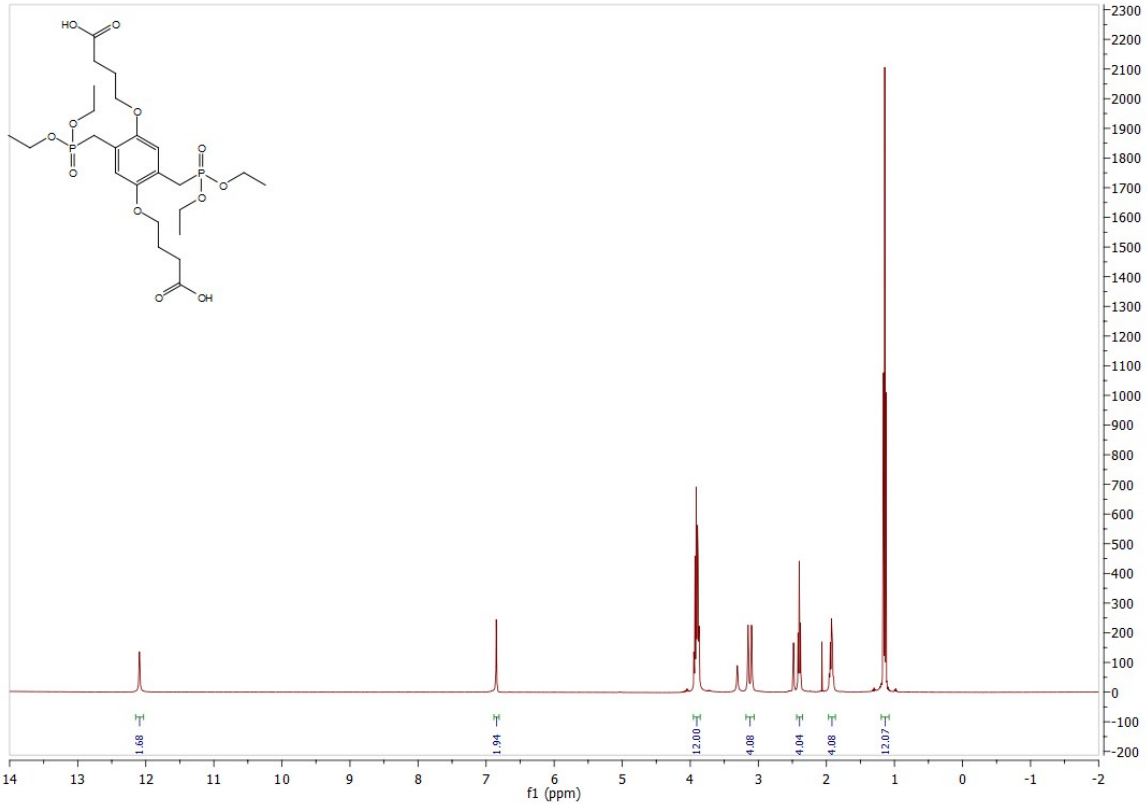


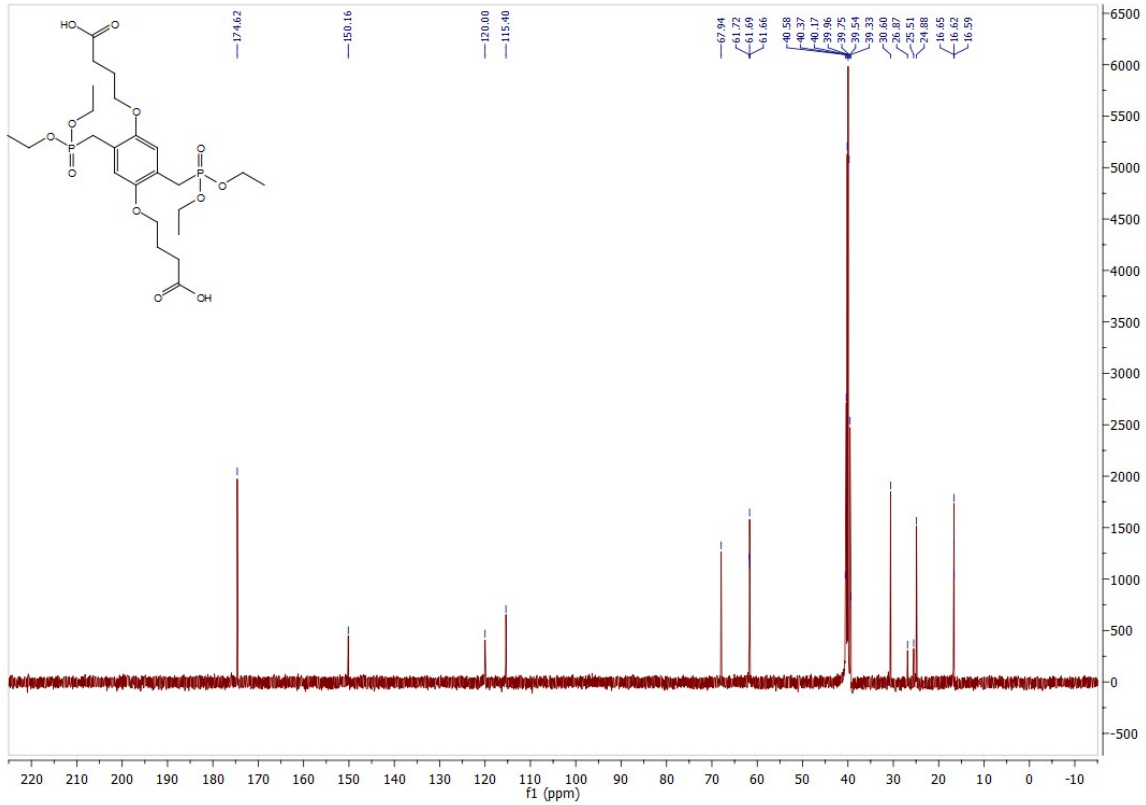
Compound II


HO
O
O
Br
Br
O
O
OH
1.44
1.73
3.49
3.97
4.00
4.11
f1 (ppm)

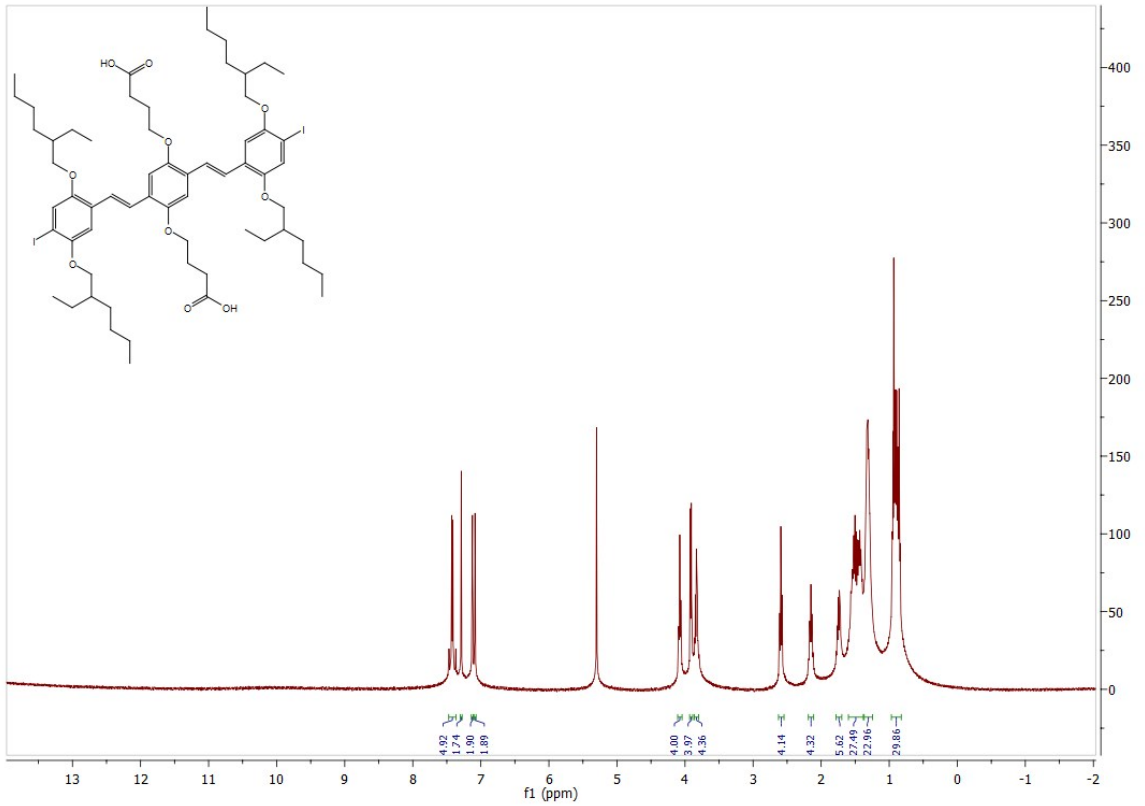

HO
O
O
Br
Br
O
O
OH
174.62
150.56
127.72
115.27
67.90
40.60
40.39
40.18
39.97
39.76
39.55
39.35
30.62
30.19
24.80
f1 (ppm)

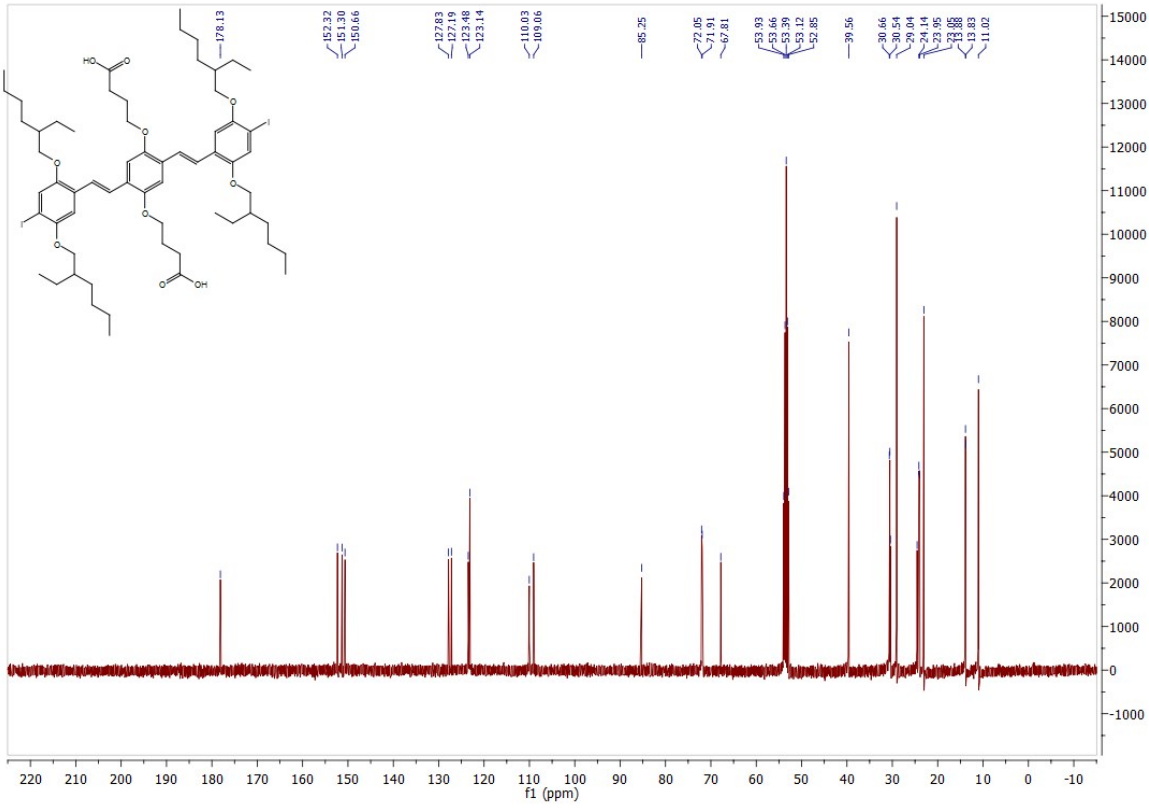
Compound 4


1.68
1.94
12.00
4.08
4.04
4.08
12.07
f1 (ppm)

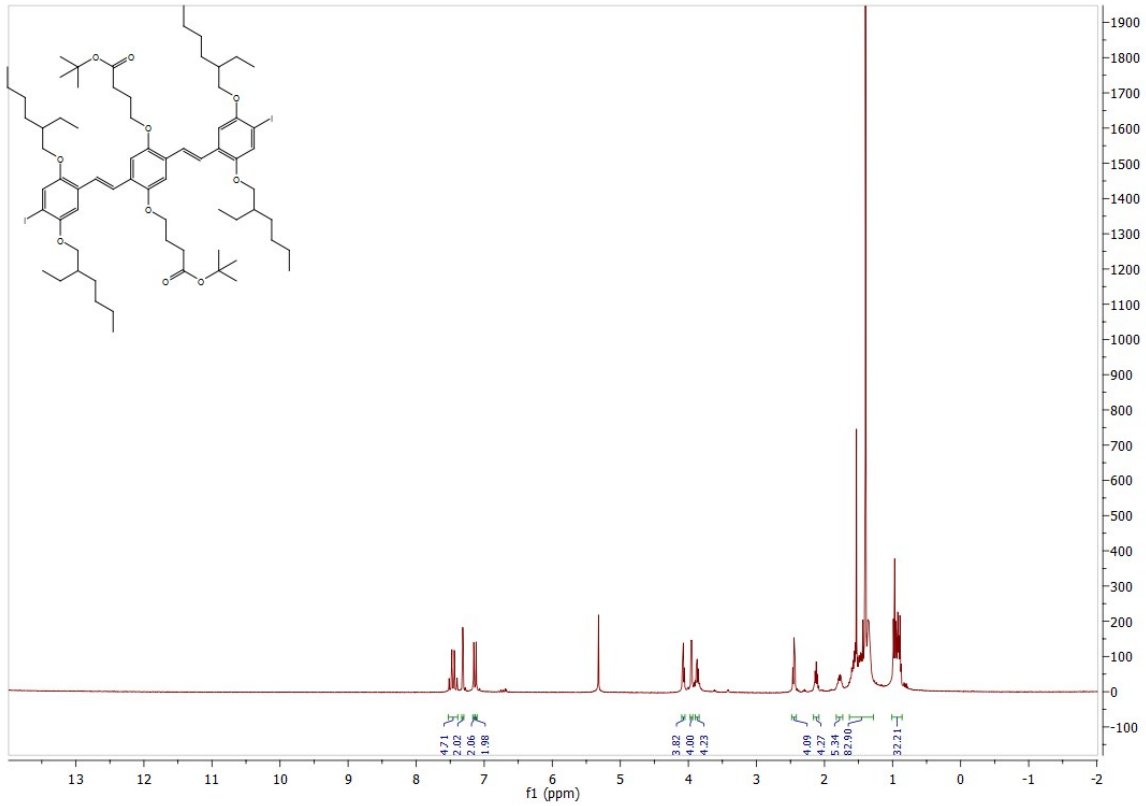

174.62
150.16
120.00
115.40
67.94
61.72
61.69
61.66
40.58
40.37
40.17
39.96
39.75
39.54
39.33
30.60
26.87
25.51
24.88
16.65
16.62
16.59
f1 (ppm)

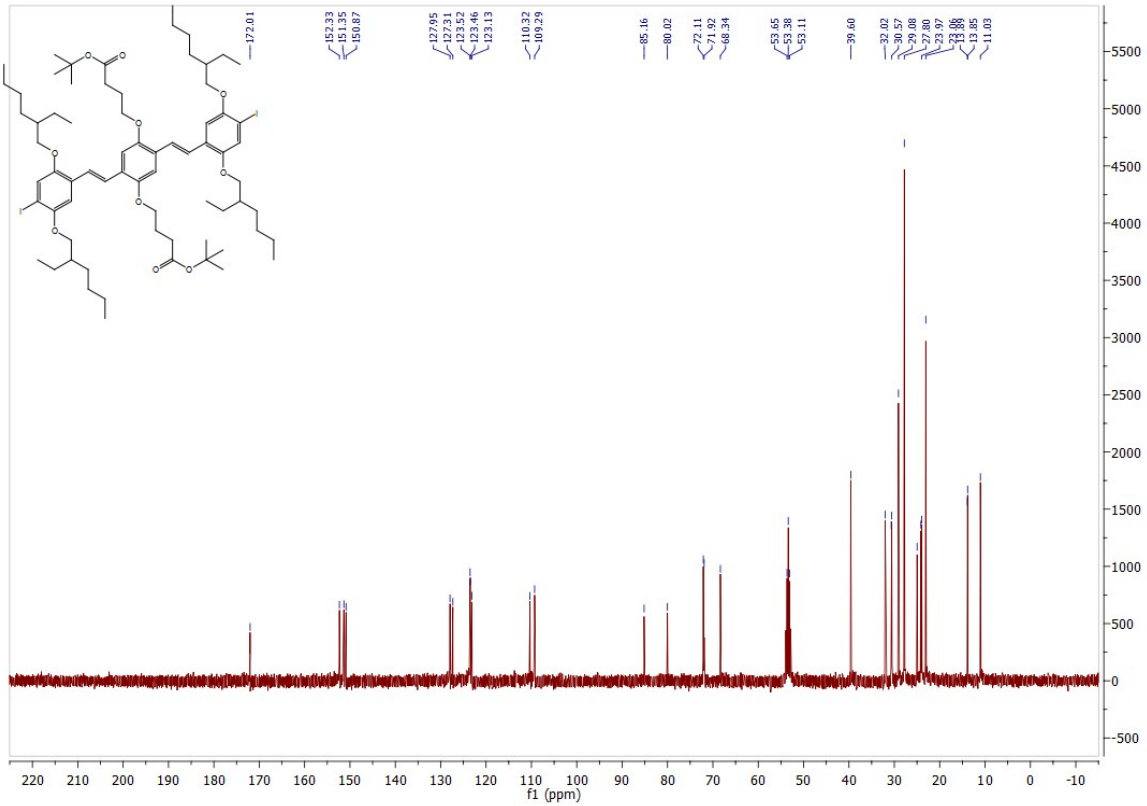
Compound 6


HO
O
O
I
O
O
I
O
O
O
O
OH
4.92
1.74
1.90
1.89
4.00
3.97
4.36
4.14
4.32
5.62
27.49
22.96
29.86
f1 (ppm)

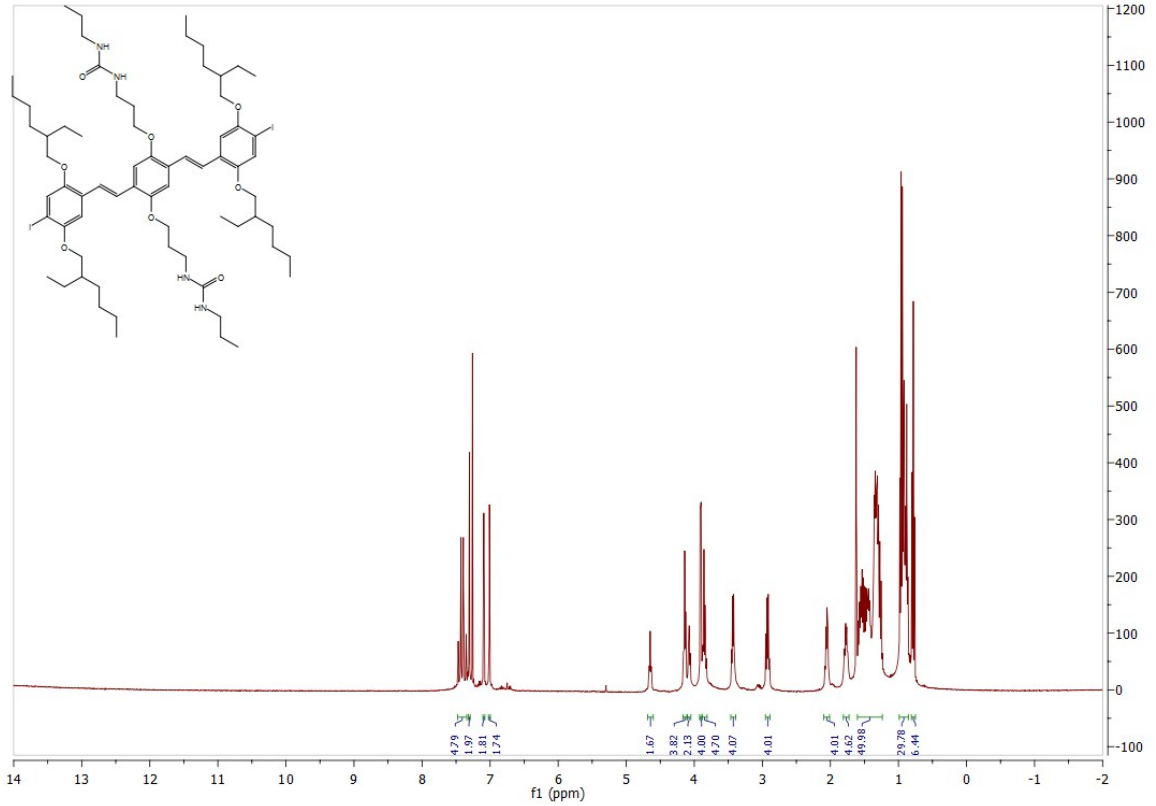

178.13
152.32
151.30
150.66
127.83
127.19
123.48
123.14
110.03
109.06
85.25
72.05
71.91
67.81
53.93
53.66
53.39
53.12
52.85
39.56
30.66
30.54
29.04
24.14
23.95
13.88
13.83
11.02
HO
O
O
I
O
O
I
O
O
O
O
OH
f1 (ppm)

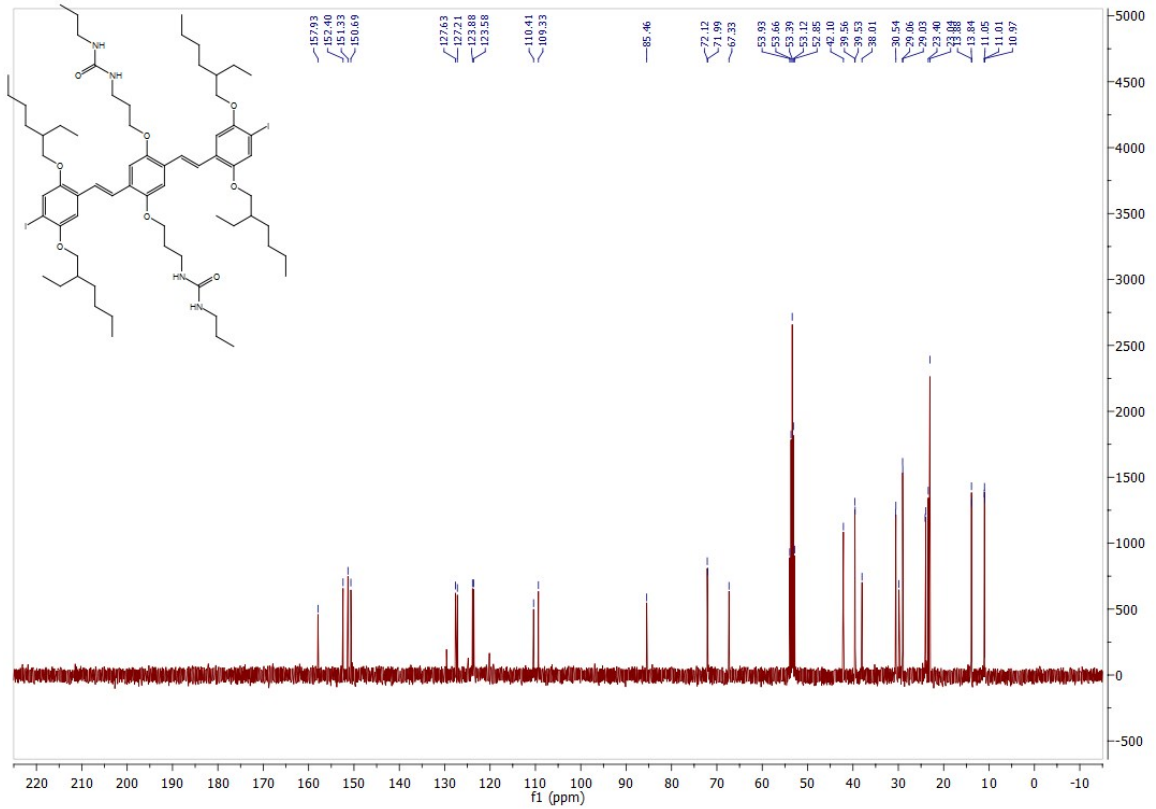
Compound 7


4.71
2.02
2.06
1.98
3.82
4.00
4.23
4.09
4.27
5.34
82.90
32.21
f1 (ppm)

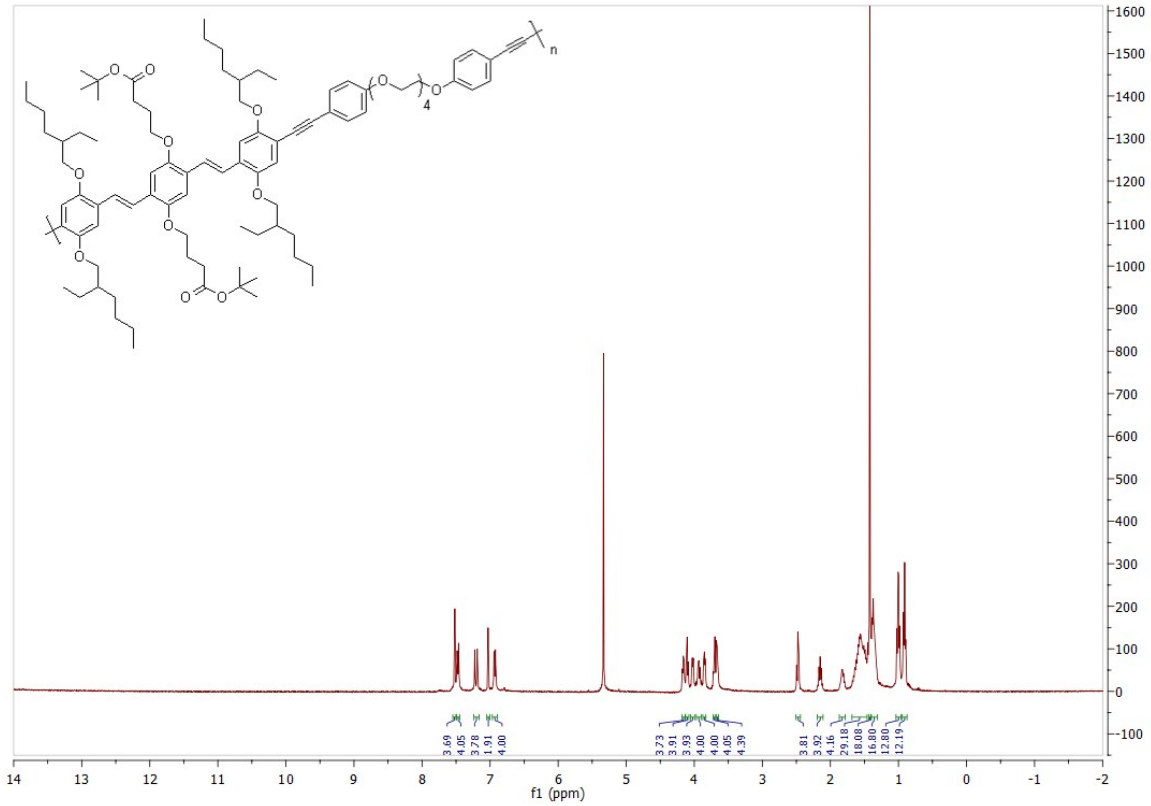

172.01
152.33
151.35
150.87
127.95
127.31
123.52
123.46
123.13
110.32
109.29
85.16
80.02
72.11
71.92
68.34
53.65
53.38
53.11
39.60
32.02
30.57
29.08
27.80
23.97
13.85
11.03
f1 (ppm)

Compound 8

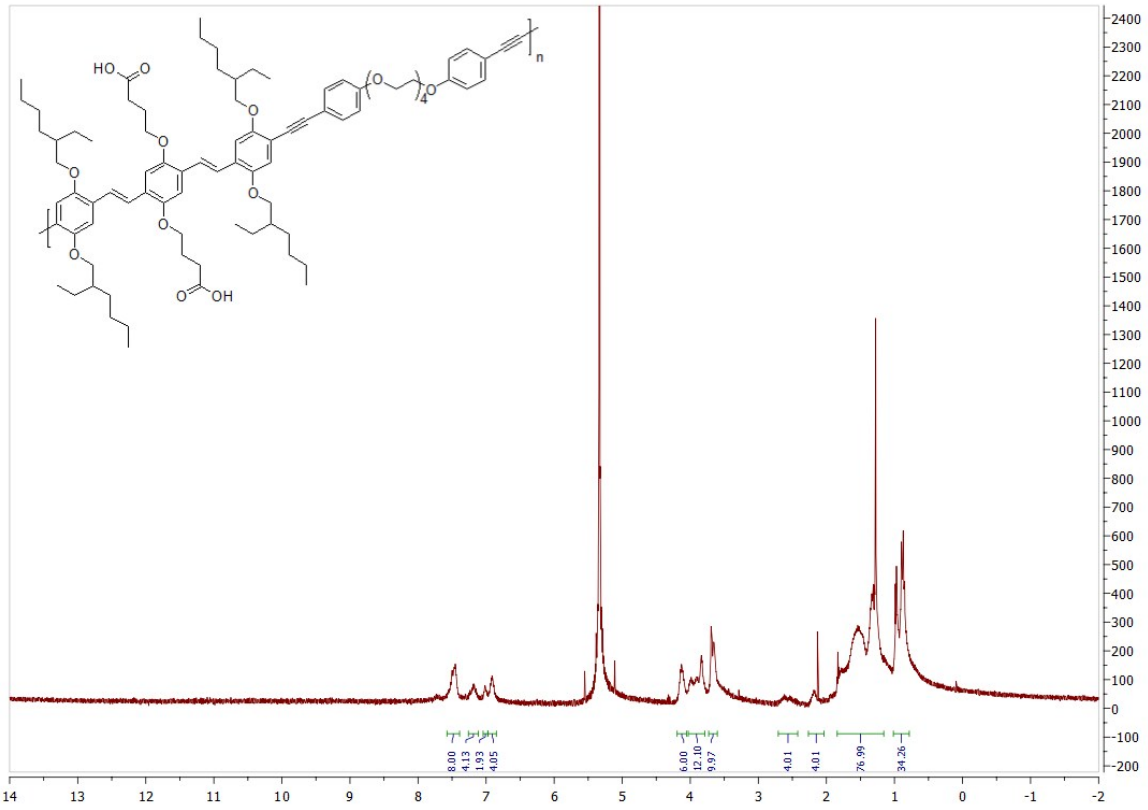

4.79
1.97
1.81
1.74
1.67
3.82
2.13
4.00
4.70
4.07
4.01
4.01
4.82
49.98
29.78
6.44
f1 (ppm)


157.93
152.40
151.33
150.69
127.63
127.21
123.88
123.58
110.41
109.33
85.46
72.12
71.99
67.33
53.93
53.66
53.39
53.12
52.85
42.10
39.56
39.53
38.01
30.54
29.06
29.03
23.40
13.84
11.05
11.01
10.97
f1 (ppm)

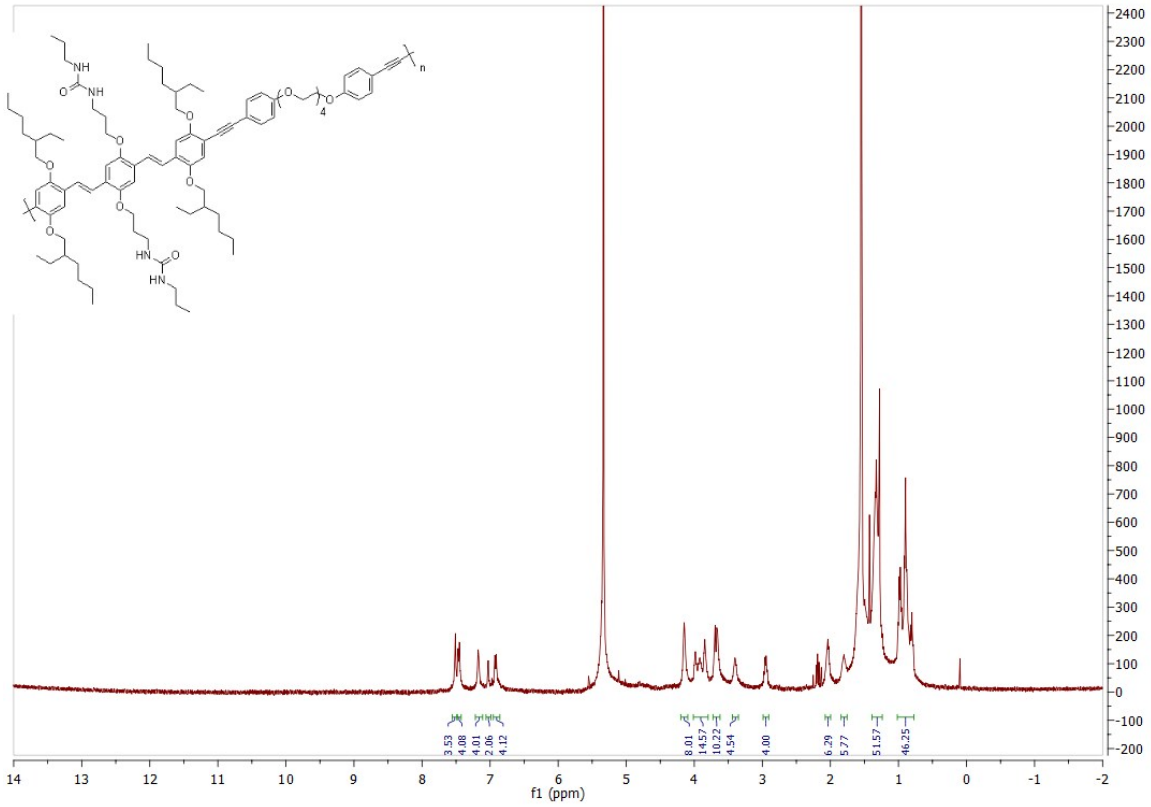
Polymer 1



Polymer 2


HO
O
O
O
O
O
O
O
O
O
O
O
O
OH
n
8.00
4.13
1.93
4.05
6.00
12.10
9.97
4.01
4.01
76.99
34.26

Polymer 3


NH
O
NH
O
O
O
O
O
O
O
O
4
n
HN
O
HN
3.53
4.08
4.01
2.06
4.12
8.01
14.57
10.22
4.54
4.00
6.29
5.77
51.57
46.25
f1 (ppm)

References:

(1) Zhu, X.; Traub, M. C.; Vanden Bout, D. A.; Plunkett, K. N. Well-Defined Alternating Copolymers of Oligo(phenylenevinylene)s and Flexible Chains. *Macromolecules* **2012**, *45* (12), 5051–5057.
(2) Pei, D.; Hong, J.; Lin, F.; Shi, Z.; Chen, Z.; Nie, H.; Guo, X. A Highly Sensitive and Selective Antioxidant Probe Based on a Bi-Modally Functionalized Conjugated Polyelectrolyte. *Chem. Commun.* **2011**, *47* (33), 9492–9494.