

## Supporting Information for

### Preparation and Characterization of Conjugated Polymers Made by Post-polymerization Reactions of Alternating Polyketones

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#### General Methods

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 400 (400 MHz) or a Bruker DRX 500 (500 MHz) spectrometer in CDCl<sub>3</sub>. IR spectra were recorded on a Bruker Alpha-p ATR spectrometer. UV-VIS spectra were recorded using a Varian Cary 300 Bio or an Agilent 8453 spectrophotometer. Thin films were cast from CH<sub>2</sub>Cl<sub>2</sub> solutions (10 mg/mL) on glass slides with a Chemat Technology Spin-coater KW-4A at 800 rpm for 30 s. The thickness of the films was determined with a Tencor Instruments alpha-step 200 profilometer. Photoluminescence was detected on a PTI QuantaMaster 40 spectrofluorometer. Molecular weights were determined against polystyrene standards using a Waters 2695 GPC system at room temperature with tetrahydrofuran as the mobile phase on three columns (Waters Styragel HR4, HR2, and HR 0.5) at a flow rate of 1 mL/min. Thermal decomposition up to 500 °C was recorded with a Perkin-Elmer Pyris 1 thermogravimetric analyzer with a heating rate of 20 °C/min under a N<sub>2</sub> flow of 20 mL/min. Glass transition temperatures were measured with a TA Q200 differential scanning calorimeter, using a heating rate of 10 °C/min and cooling rate of 20 °C/min ranging 25 - 200 °C. Cyclic voltammetry (CV) was conducted using a Bioanalytical Systems Epsilon Electrochemical Analyzer with a standard three-electrode electrochemical cell in a tetrabutylammonium hexafluorophosphate solution in CH<sub>3</sub>CN at room temperature with a scanning rate of 0.1 V/s. A glassy carbon working electrode, a Pt wire counter electrode, and an Ag/AgCl (0.01 M in CH<sub>3</sub>CN) reference electrode were used. A thin film of polymer was coated on the working electrode before each scan. The CV results were referenced with the standard ferrocene/ferrocenium redox system.

#### Polymerizations

Poly(4-*tert*-butylstyrene-alt-CO) (p(<sup>t</sup>BuS-CO)) and poly(styrene-alt-CO) (p(S-CO)) were prepared using palladium catalysts according to the literature.<sup>1</sup> Poly(4-chlorostyrene-alt-CO), and poly(4-fluorostyrene-alt-CO) were prepared in a similar manner. Isotactic p(<sup>t</sup>BuS-<sup>13</sup>CO) was prepared using a C<sub>2</sub> bisoxazoline palladium catalyst following the literature procedure.<sup>2</sup>

## Modifications

### *Modification on p(<sup>t</sup>BuS-CO) films*

A thin film of p(<sup>t</sup>BuS-CO) was drop cast on the bottom of a scintillation vial from a CH<sub>2</sub>Cl<sub>2</sub> solution (100 mg/mL). Three drops of bromine was dropped on the cap, and the vial was inversely capped. After one day, the remaining bromine was allowed to evaporate to give a dark red neutral p(<sup>t</sup>BuS-CO) **3**.

### *Modification in solution with gaseous acids*

Polymers **1** (Ar = -C<sub>6</sub>H<sub>5</sub>, -C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>3</sub>, -C<sub>6</sub>H<sub>4</sub>Cl) were dissolved or suspended in CH<sub>2</sub>Cl<sub>2</sub>, and HCl or HBr gas was purged through the solution for 10 min. Gradual color change was observed during the period. After the reaction mixture had been stirred for one day, the acid and solvent were removed to give dark blue acid-doped polymers **2**.

### *Modification in solution with liquid acids*

Polymers **1** (Ar = -C<sub>6</sub>H<sub>5</sub>, -C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>3</sub>, -C<sub>6</sub>H<sub>4</sub>Cl) were dissolved or suspended in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> in a scintillation vial, and to the vial was added various acids (CH<sub>3</sub>SO<sub>3</sub>H, CF<sub>3</sub>SO<sub>3</sub>H, H<sub>2</sub>SO<sub>4</sub>). After stirring for one day, the mixture was diluted with 40 mL of CH<sub>2</sub>Cl<sub>2</sub>, extracted with 2 × 20 mL of 38% aqueous NH<sub>4</sub>OH solution, dried over MgSO<sub>4</sub>, and the solvent was removed to give orange neutral polymers **2**.

### *Bromination of acid-modified polymer with NBS*

A typical bromination/elimination reaction was carried out as follows: In 20 mL degassed chloroform was dissolved p(<sup>t</sup>BuS-CO) **2** (500 mg, 1.40 mmol repeating units), *N*-bromosuccinimide (249 mg, 1.40 mmol), and azobisisobutylnitrile (23 mg, 0.14 mmol), and the reaction mixture was heated at reflux for 4 hr. Then the reaction mixture was diluted with 40 mL chloroform, extracted with 2 × 20 mL 2 M NaOH, dried over MgSO<sub>4</sub>, filtered, and from the filtrate was recovered the dark red neutral p(<sup>t</sup>BuS-CO) **3**.

### *One-pot bromination/elimination reaction*

A typical one-pot reaction with bromine to generate **3** was carried out as follows: To a suspension of p(S-CO) **1** (484 mg, 2.00 mmol repeating units) in 10 mL chloroform was added bromine (380 mg, 2.38 mmol). The mixture was stirred for 5 min at room temperature (during which it turned dark blue) then heated at reflux for 4 hr. The reaction mixture was diluted with 40 mL chloroform, extracted with 2 × 20 mL 2 M NaOH, dried over MgSO<sub>4</sub>, filtered, and the solvent was removed to give the dark purple neutral p(S-CO) **3**.

## Calculations

### *Determination of conversion*

Since the benzylic proton (proton on C3, 3.75-4.25 ppm) is present in both **1** and **2** whereas the vinylic proton (proton on C1, 6 ppm) is specific for structure **2**, and since two polyketone repeating units in **1** form one conjugated repeating unit in **2**, the degree of conversion for the p(<sup>t</sup>BuS-CO) sample in Figure S11 was determined by as follows:

$$\begin{aligned}\text{conversion} &= \frac{2 \times \text{modified moieties}}{2 \times \text{modified moieties} + \text{unmodified moieties}} \\ &= \frac{2 \times \text{vinyl H}}{2 \times \text{vinyl H} + (\text{benzylic H} - \text{vinyl H})} = \frac{2 \times 0.74}{2 \times 0.74 + (1 - 0.74)} = 85\%\end{aligned}$$

This degree of conversion agrees with irreversible condensation reactions on a polymer chain, the maximum conversion of monomer units is 86%, assuming all condensations occur at equal rate and also correlates with the elemental analysis result for this sample (Table S2).

## Acknowledgments

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## References

- (1) Rix, F. C.; Rachita, M. J.; Wagner, M. I.; Brookhart, M. Milani, B.; Barborak, J. C. *Dalton Trans.* **2009**, 8977.
- (2) Brookhart, M.; Wagner, M. I.; Balavoine, G. G. A.; Haddou, H. A. *J. Am. Chem. Soc.* **1994**, *116*, 3641.

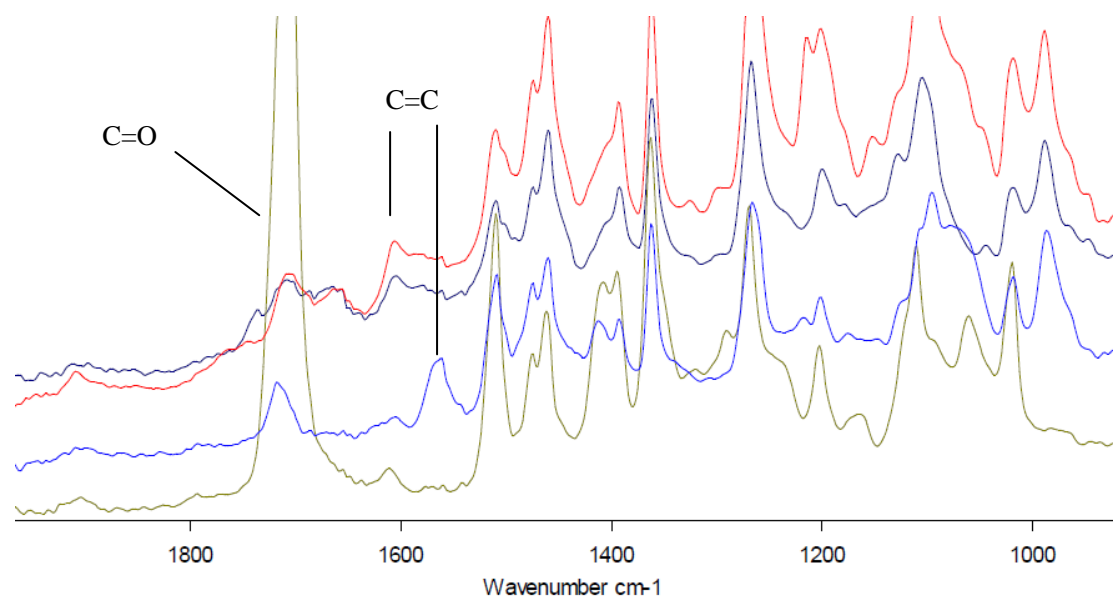
## Tables and Graphs



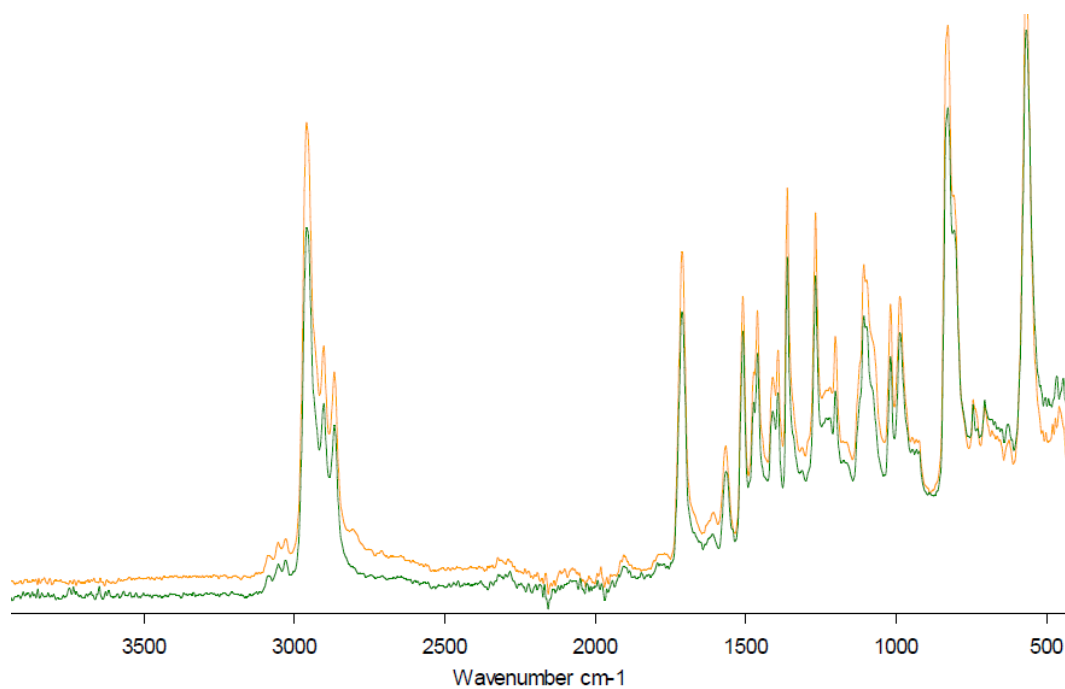
Starting material      Immediately after acid addition      5 min      10 min      30 min      12 hr, 10X dilution (right)

**Figure S1.** p(<sup>t</sup>BuS-CO) **1** modification with MeSO<sub>3</sub>H. Photos taken at indicated time. Condition: 20 mg p(<sup>t</sup>BuS-CO) **1** and 25 mg MeSO<sub>3</sub>H in 10 mL CH<sub>2</sub>Cl<sub>2</sub>.

IR

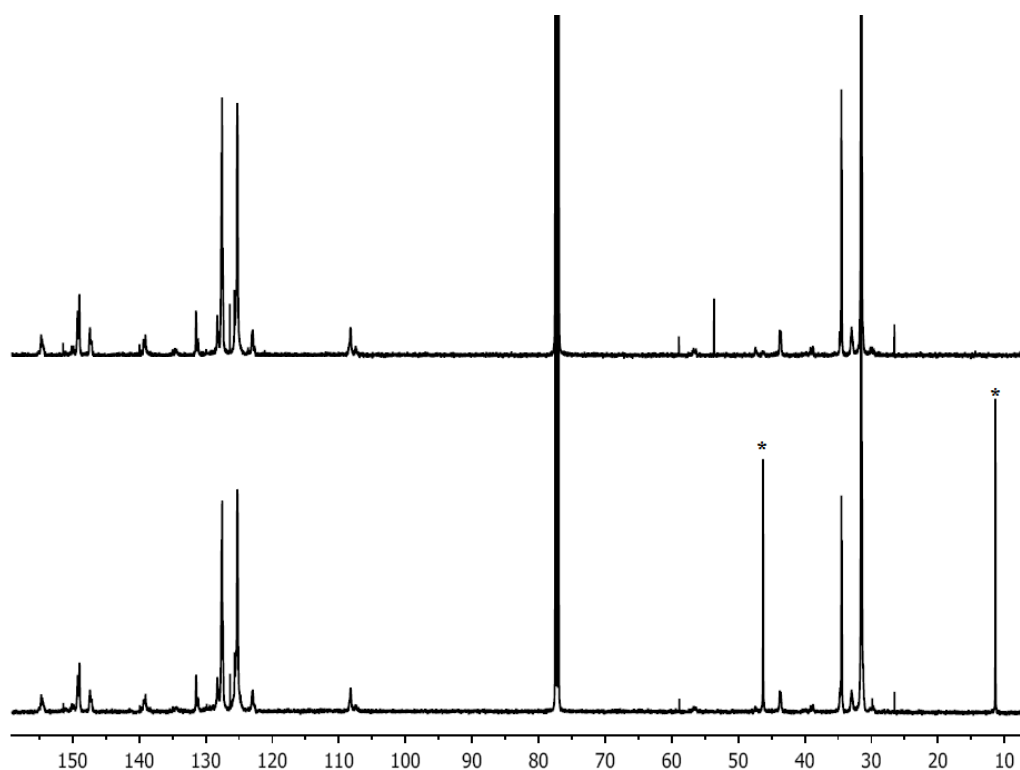


**Figure S2.** Comparison of the carbonyl and C=C regions of p(<sup>t</sup>BuS-CO) **1** (grey), **2** (blue), and **3** (red, from NBS reaction of **2**, and purple, from Br<sub>2</sub> one-pot reaction of **1**).

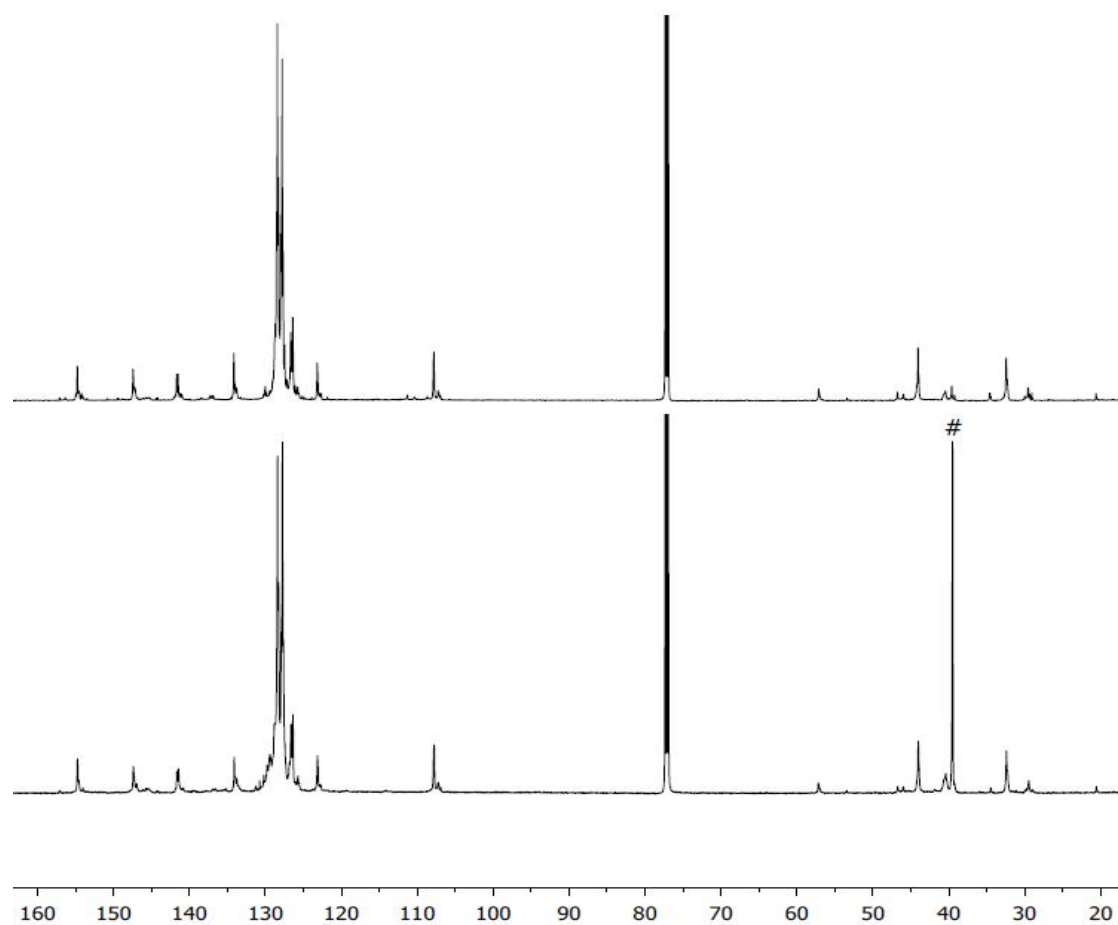


**Figure S3.** IR spectra of doped (green line) and neutral (yellow line) p'(BuS-CO) **2**. The almost identical spectra suggest the same structure.

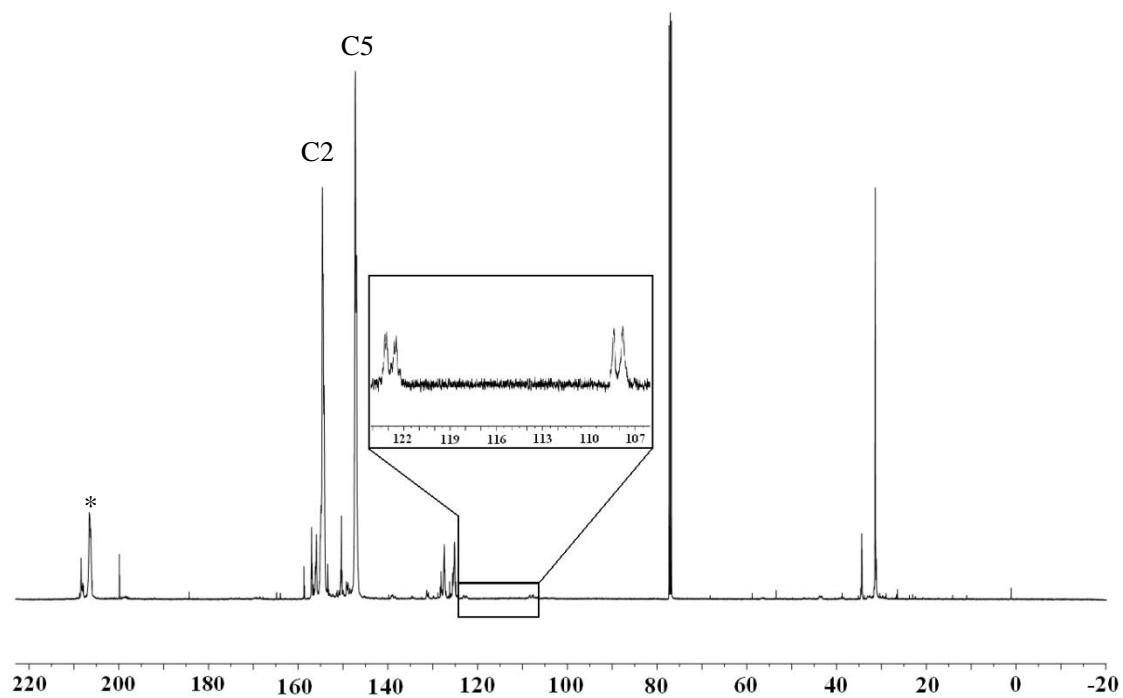
#### NMR



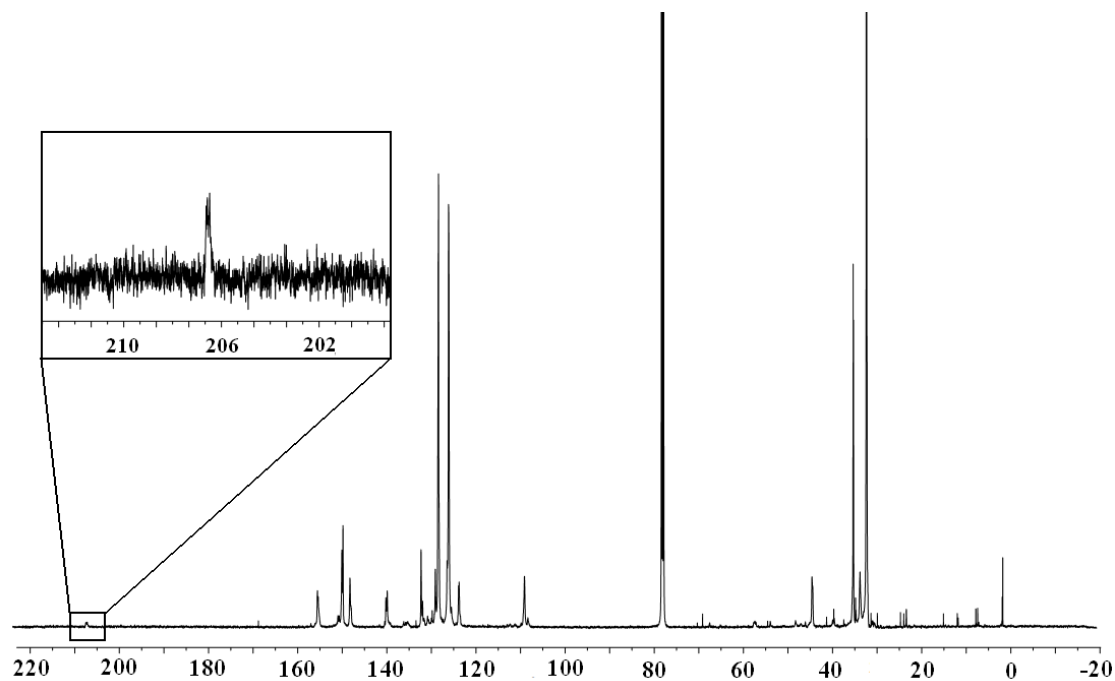
**Figure S4.**  $^{13}\text{C}$  NMR spectra of isotactic p'(BuS-CO) **2** doped with HCl gas (upper spectrum) and the same sample after neutralization using triethylamine (lower spectrum, residual  $\text{Et}_3\text{N}$  mark with “\*”).



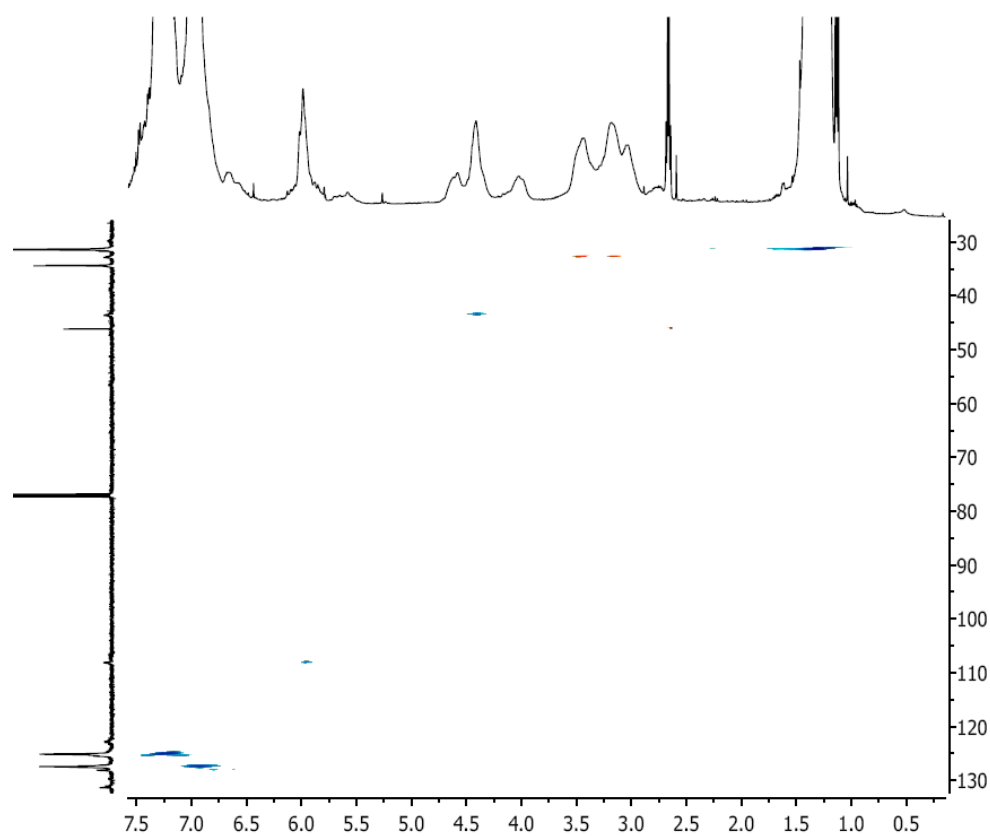
**Figure S5.**  $^{13}\text{C}$  NMR spectra of p(S-CO) **2** neutral (upper spectrum) and the same sample after doping with methanesulfonic acid (lower spectrum, signal from acid marked with “#”).



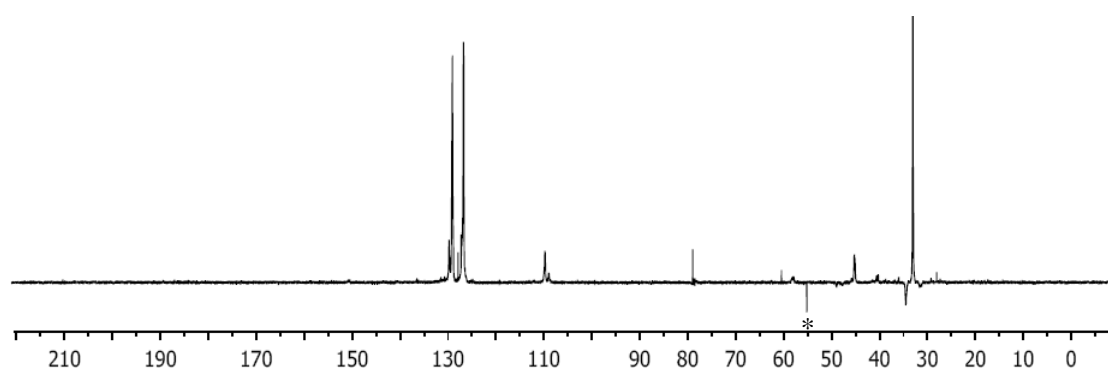
**Figure S6.**  $^{13}\text{C}$  NMR spectrum of  $p(t\text{BuS-CO})$  **2** prepared with  $^{13}\text{CO}$ . (\* residual ketone signal)



**Figure S7.**  $^{13}\text{C}$  NMR spectrum of  $p(t\text{BuS-CO})$  **2** with residual ketone shown.

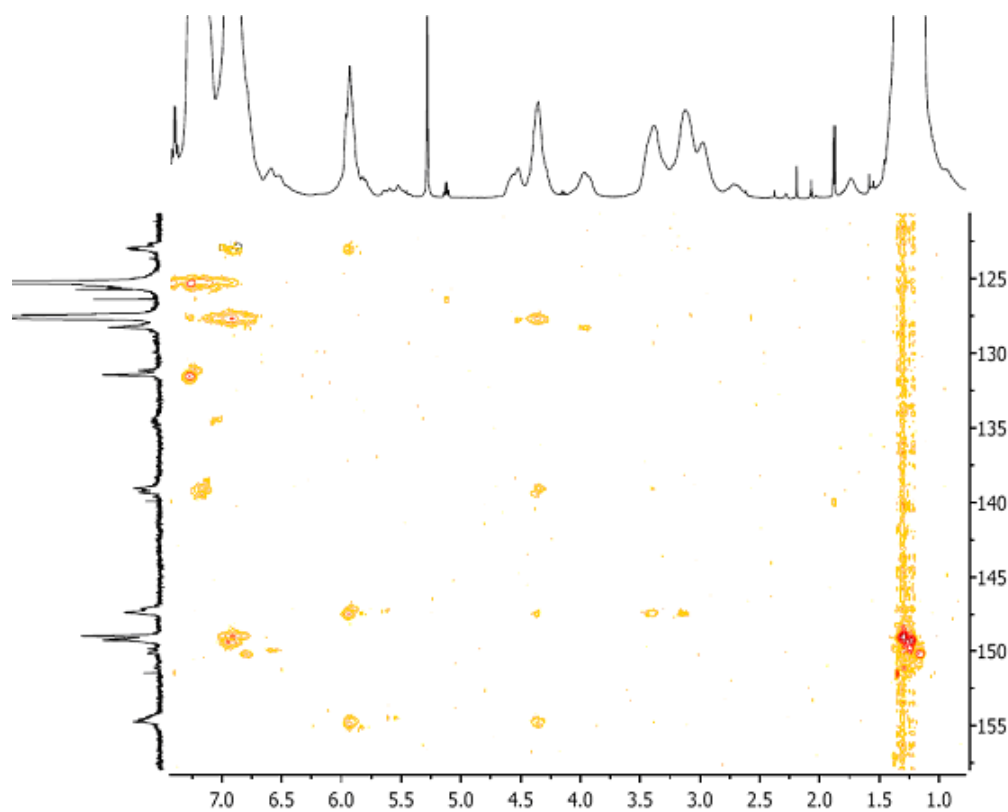


**Figure S8.** Phase sensitive gHSQC of isotactic p(<sup>t</sup>BuS-CO) **2**; blue: methyl and methyne, red: methylene.

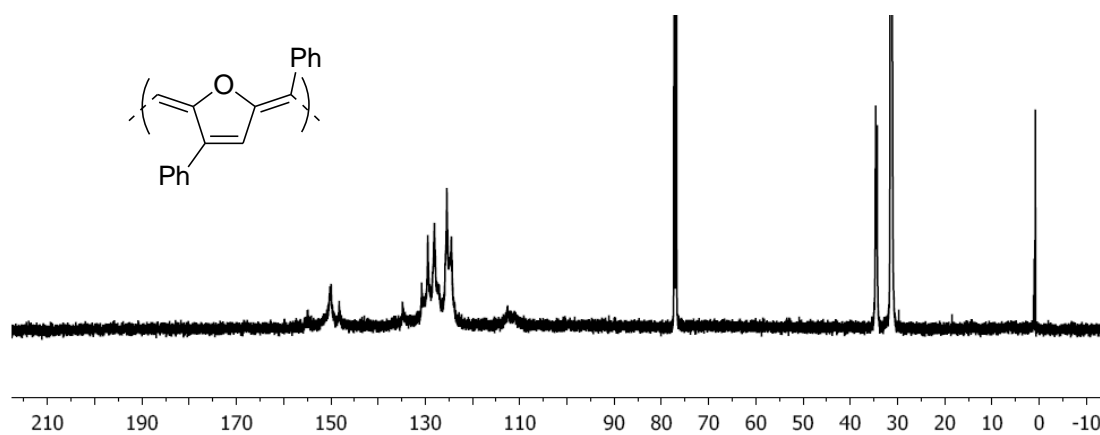


**Figure S9.** <sup>13</sup>C DEPT-135 of isotactic p(<sup>t</sup>BuS-CO) **2**, with methylene carbon signals pointing down, methyl and methyne signals pointing up. (\* CH<sub>2</sub>Cl<sub>2</sub>)

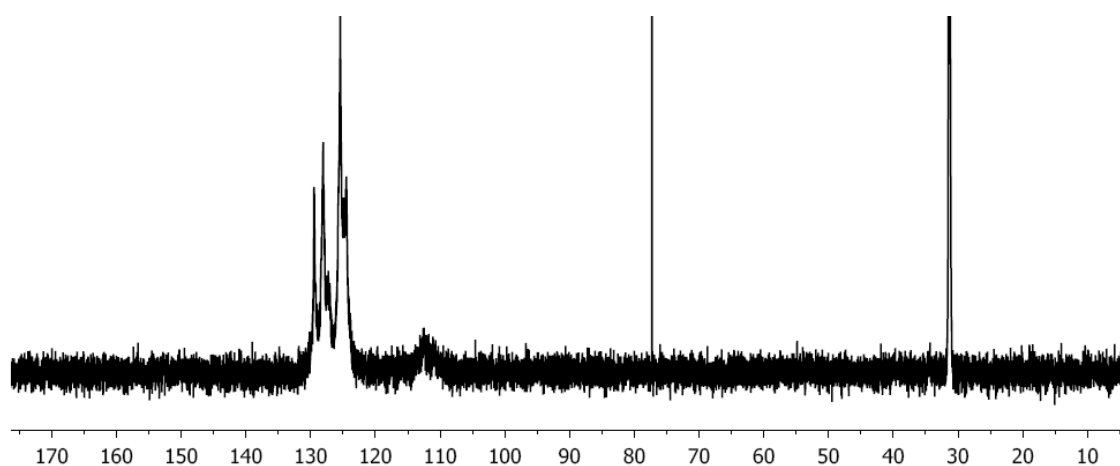




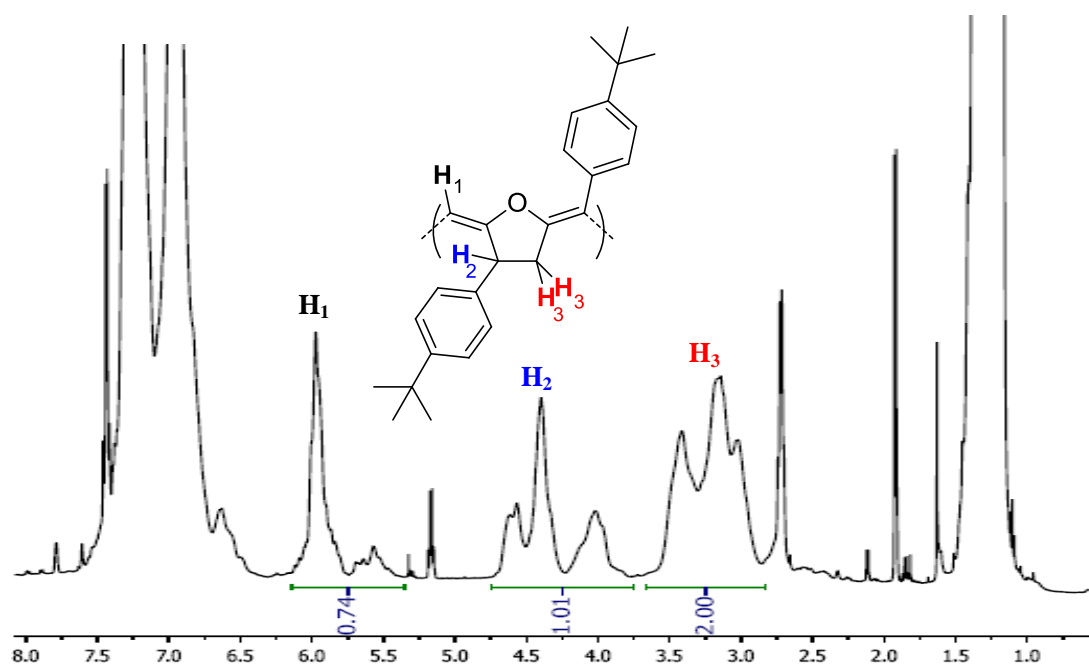
**Figure S10.** gHMBC of isotactic p(<sup>t</sup>BuS-CO) **2**; low field carbon region.



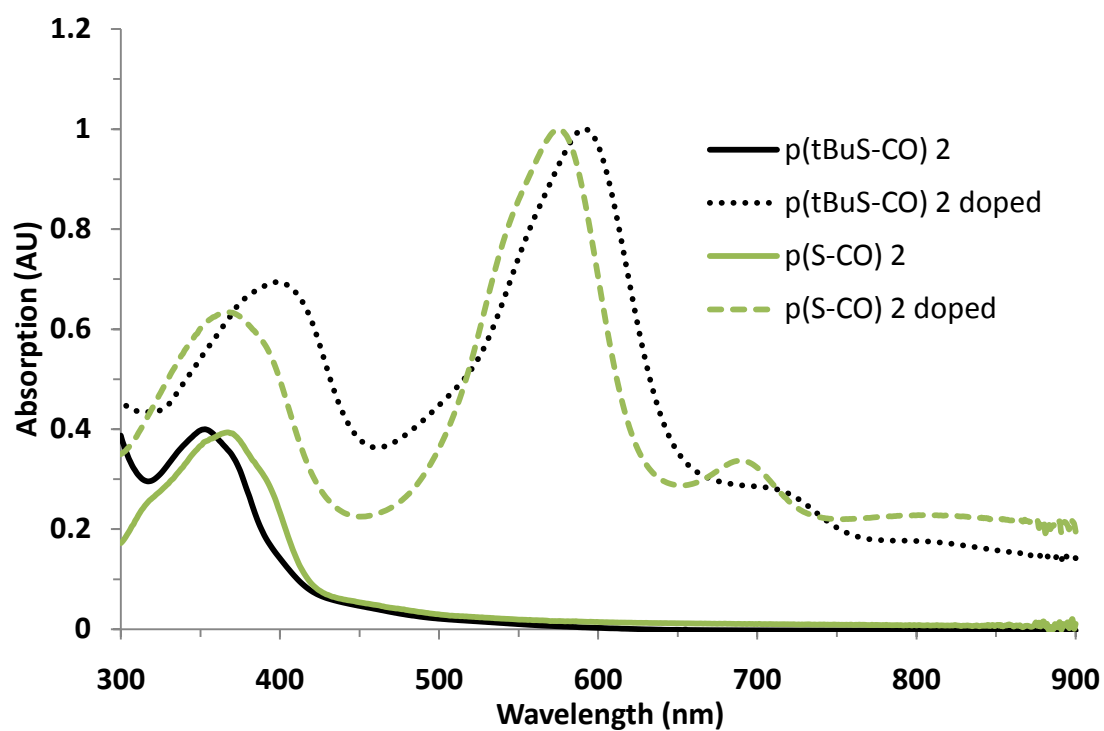
**Figure S11.**  $^{13}\text{C}$  NMR of p(<sup>t</sup>BuS-CO) **3**.



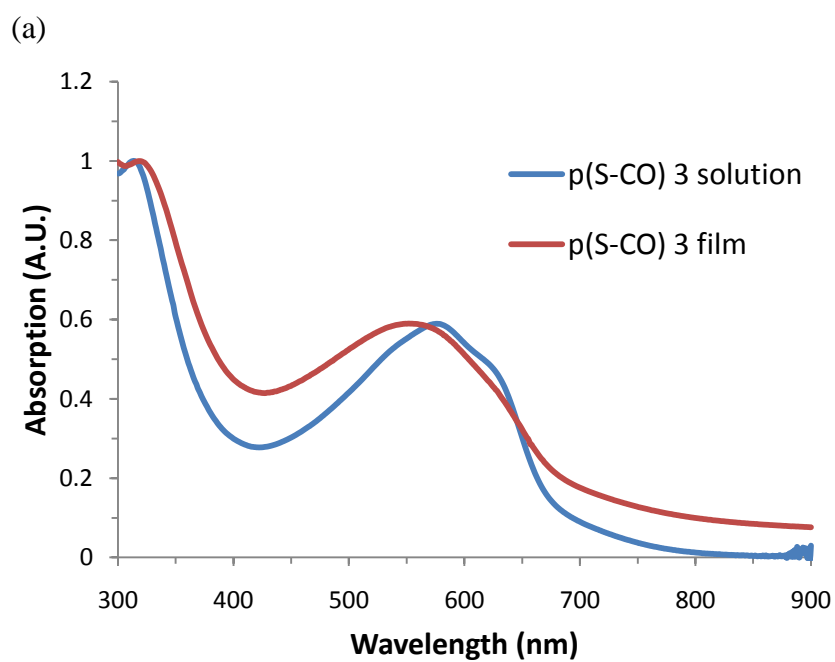
**Figure S12.**  $^{13}\text{C}$  DEPT-135 NMR of  $p(4\text{BuS-CO})$  **3**; one broad methyne carbon at 110ppm must be a vinyl carbon.

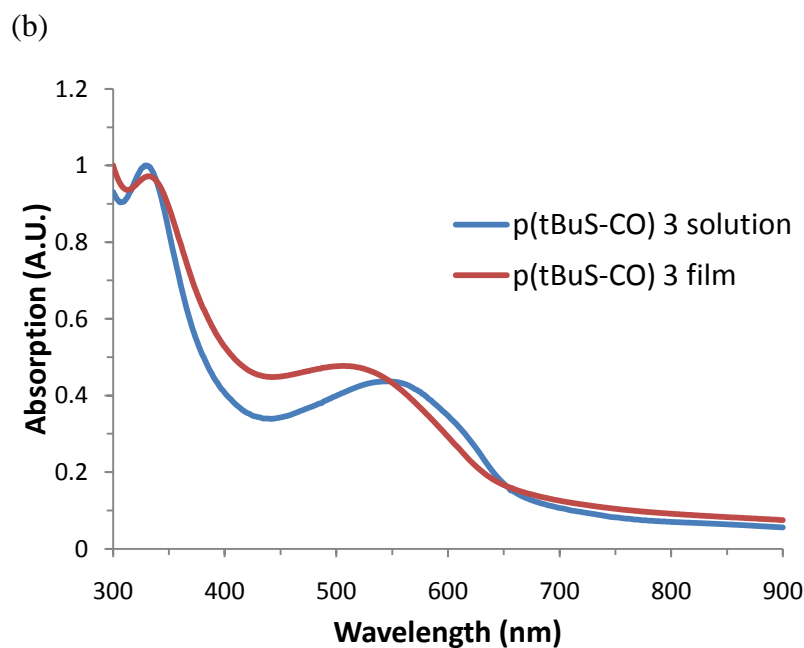


**Figure S13.**  $^1\text{H}$  NMR spectrum used to determine degree of modification for HBr modified  $p(4\text{BuS-CO})$  **2**.



**Figure S14.** Neutral and acid doped p(S-CO) 2 and p(*t*BuS-CO) 2.





**Figure S15.** UV-Vis absorption of solution and film of neutral (a) p(S-CO) **3** and (b) p(<sup>t</sup>BuS-CO) **3**.

**Table S1.** UV-Vis absorption data of the modified polyketones.

Entry	Polymer	$\lambda_1^a$ (nm)	$\lambda_2^a$ (nm)	$\lambda_1^b$ (nm)	$\alpha_1$ ( $10^5 \text{ cm}^{-1}$ )	$\lambda_2^b$ (nm)	$\alpha_2$ ( $10^5 \text{ cm}^{-1}$ )
1-1	p( <sup>t</sup> BuS-CO) <b>2</b>	353	-	352s <sup>c</sup>	0.029	-	-
1-2	p( <sup>t</sup> BuS-CO) <b>2</b> (d) <sup>d</sup>	401	591	- <sup>e</sup>	-	-	-
1-3	p( <sup>t</sup> BuS-CO) <b>2</b> (d)	368	575	-	-	-	-
1-4	p( <sup>t</sup> BuS-CO) <b>3</b> <sup>f</sup>	329	551	334	0.33	517	0.16
1-5	p( <sup>t</sup> BuS-CO) <b>3</b>	327	553	331	0.30	506	0.14
1-6	p( <sup>t</sup> BuS-CO) <b>3</b> (d)	328	935	-	-	-	-
1-7	p(S-CO) <b>3</b>	313	577	317	0.46	545	0.24
1-8	p(S-CO) <b>3</b> (d)	324	960	-	-	-	-
1-9	p(CIS-CO) <b>3</b>	328s	569	330	0.40	550	0.22
1-10	p(FS-CO) <b>3</b>	310	570	310s	0.32	540	0.23

<sup>a</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>b</sup> Spin-coated on glass slides. <sup>c</sup> Shoulder. <sup>d</sup> Polymer doped with MeSO<sub>3</sub>H. <sup>e</sup> Not determined since MeSO<sub>3</sub>H doped polymer cannot be obtained in neat solid state. <sup>f</sup> Modified from p(<sup>t</sup>BuS-CO) **2** with NBS. All other **3**'s are modified from the corresponding **1**'s with bromine.

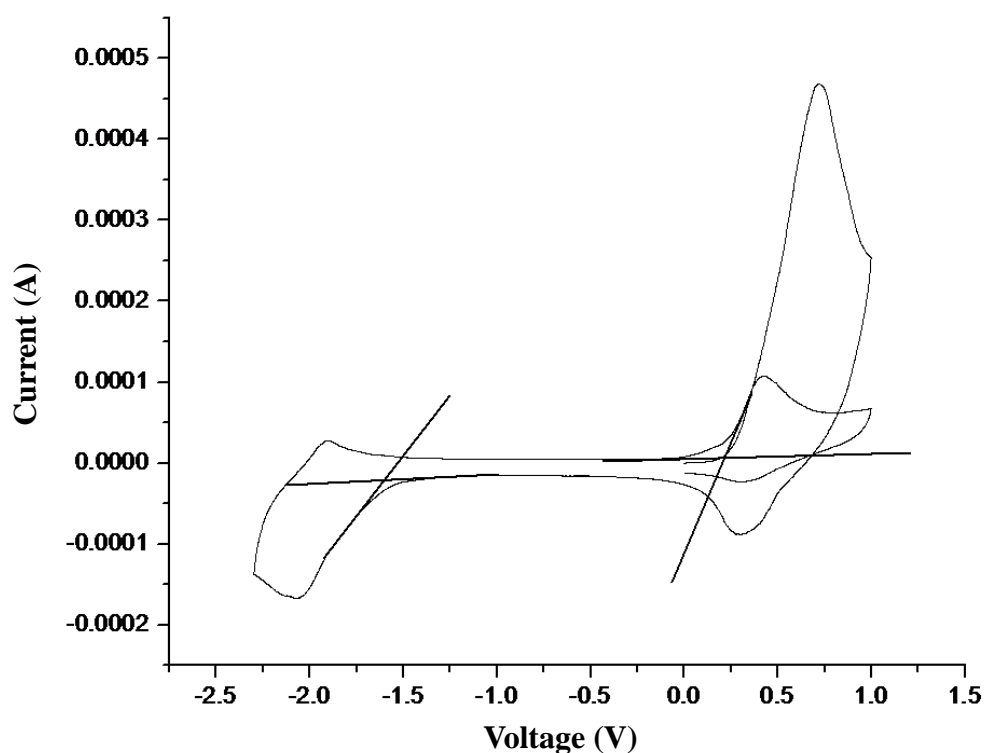
## Elemental analysis

**Table S2.** Elemental analysis data for neutral p(S-CO) **2** and p(<sup>t</sup>BuS-CO) **3**.

Sample	C (%)	H (%)	O (%)	Br (%)	Other (%)
p(S-CO) <b>1</b> theoretical	81.8	6.1	12.1	0	0
p(S-CO) <b>2</b> theoretical 85% <sup>a</sup>	86.8	5.7	7.7	0	0
p(S-CO) <b>2</b> experimental <sup>b</sup>	86.0	5.3	8.3 <sup>c</sup>	<b>0.28</b>	N: <0.02 Cl: 0.08
p( <sup>t</sup> BuS-CO) <b>3</b> <sup>d</sup>	85.2	7.6	-	<b>0.5</b>	N: 0.3
p( <sup>t</sup> BuS-CO) <b>3</b> <sup>e</sup>	86.1	7.0	-	<b>1.0</b>	N: 0.05

<sup>a</sup> At 85% conversion. <sup>b</sup> Modified with HBr gas. Degree of conversion for this sample determined by <sup>1</sup>H NMR is 85%. <sup>c</sup> Assuming all other weight is from oxygen. <sup>d</sup> Modified with NBS starting from p(<sup>t</sup>BuS-CO) **2**. <sup>e</sup> One-pot reaction with bromine starting from p(<sup>t</sup>BuS-CO) **1**.

## CV

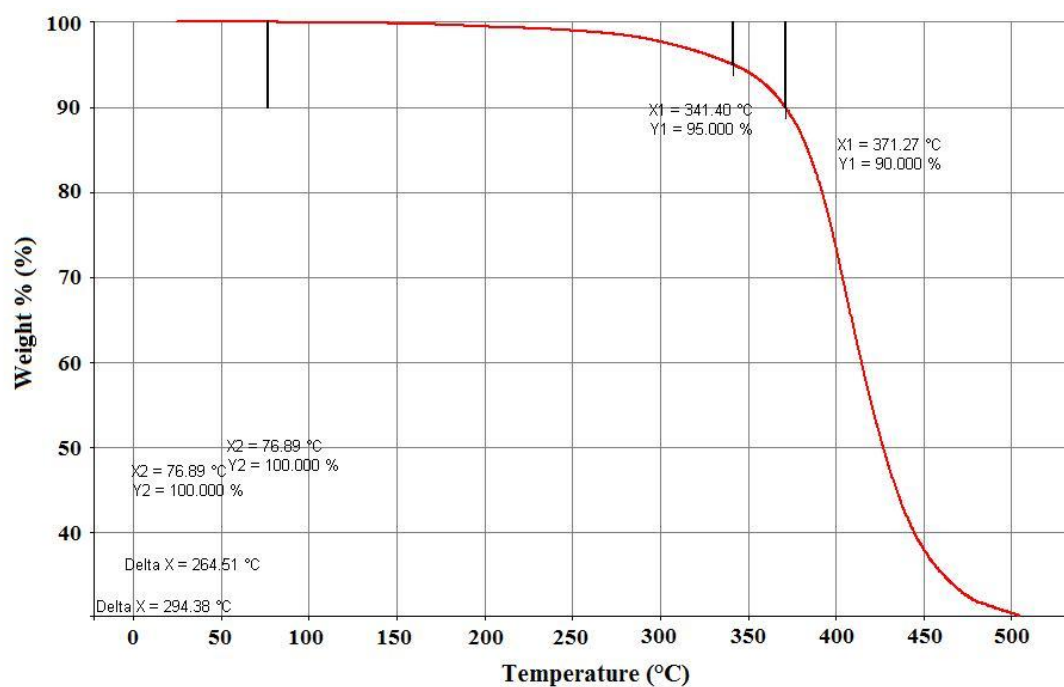


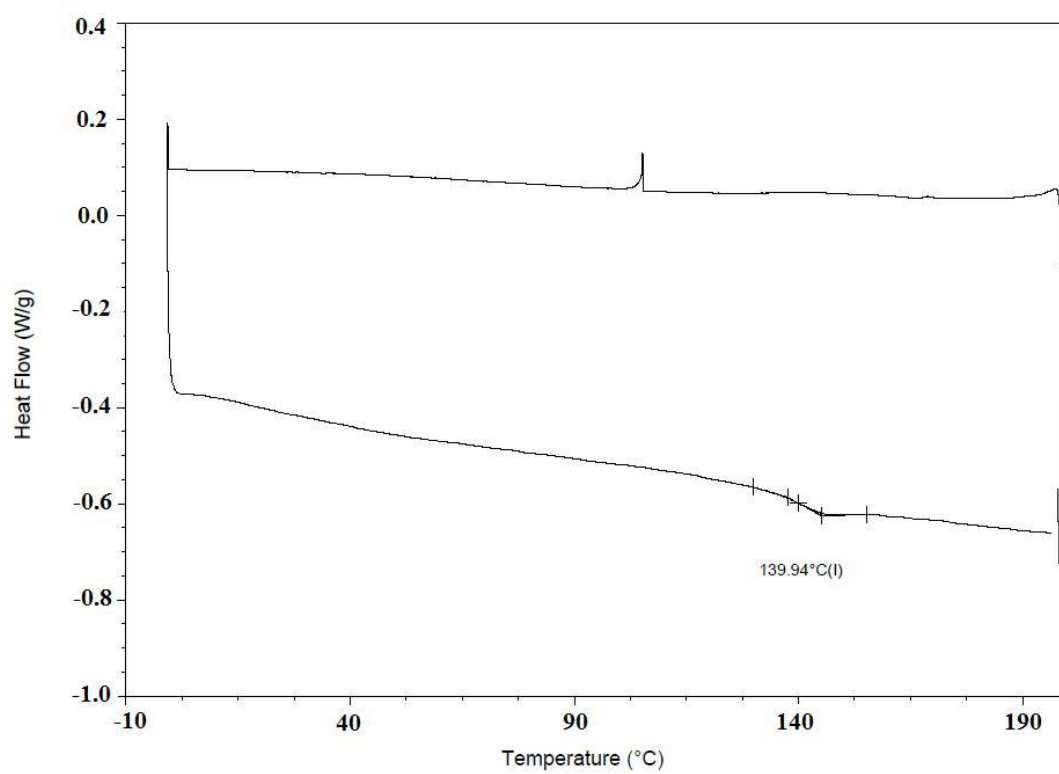
**Figure S16.** Cyclic voltammetry graph of neutral p(S-CO) **3**.

**Table S3.** Thermal properties of the neutral polymers.

Entry	Monomer	T <sub>g</sub> (°C)	5% decomposition (°C)	10% decomposition (°C)	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>
3-1	p( <sup>t</sup> BuS-CO) <b>2</b>	140	341	371	varies	-
3-2	p(S-CO) <b>2</b>	91	338	363	varies	-
3-3	p( <sup>t</sup> BuS-CO) <b>3</b>	180	375	424	17100	1.66
3-4	p(S-CO) <b>3</b>	185	418	444	28300	3.37
3-5	p(CIS-CO) <b>3</b>	-	398	439	9600	2.41
3-6	p(FS-CO) <b>3</b>	-	355	402	15300	3.16

(p(<sup>t</sup>BuS-CO) **1** T<sub>g</sub> = 114 °C, p(S-CO) **1** T<sub>g</sub> = 110 °C)

**Figure S17.** TGA of p(<sup>t</sup>BuS-CO) **2**.



**Figure S18.** DSC of p(tBuS-CO) 2.