

## SUPPORTING INFORMATION

### **RAFT polymerization of an alkoxyamine bearing acrylate, towards a well-defined redox active polyacrylate**

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## EXPERIMENTAL SECTION:

### Materials :

Acryloyl chloride (MA, 99%) was purchased from Aldrich and purified by distillation. Dichloromethane was dried and stored under argon. 4-Hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (H-TEMPO) and all other reagents, including (1-bromoethyl)benzene, Cu<sup>0</sup> powder (75 μm), CuBr, N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA), bi-pyridine, 2,2-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V70), 2-Dodecylsulfanylthiocarbonyl- sulfanyl-2-methylpropionic acid (DMP), tetrabutylammonium perchlorate (TBAClO<sub>4</sub>) and solvents were purchased from Aldrich with the highest purity available and used as received without further purification.

### Instrumentation:

<sup>1</sup>H NMR spectra of the synthesized material were recorded on a Bruker advance 250 MHz spectrometer using CDCl<sub>3</sub> as solvent. Molar mass and dispersity of the polymers were determined by size exclusion chromatography (SEC) in THF at 45°C at a flow rate of 1 mL/min with SFD S5200 autosampler liquid chromatograph equipped with a SFD refractometer index detector 2000. PL gel 5μm (10<sup>5</sup> Å, 10<sup>4</sup> Å, 10<sup>3</sup> Å and 100 Å) columns were calibrated with polystyrene standards. UV-visible spectra were recorded using a Hitachi spectrometer (U-3300) with a scan rate of 500 nm min<sup>-1</sup>. EQCM measurements were performed with a Q-sense E4 instrument using gold sensor as a working electrode, a platinum disc serving as the counter electrode, and a “no leak” Ag/AgCl electrode (Cypress Systems) was used as reference electrode. Thermogravimetric analysis (TGA) was performed under oxygen from room temperature to 600 °C with a Hi-Res TGA Q500 from TA Instruments at a heating rate of 5 °C/min.

The detailed descriptions of the QCM technique have been well documented. The changes in the fundamental resonant Δf, of a gold coated quartz crystal can be converted into a mass change, Δm (ng cm<sup>-2</sup>) via the Sauerbrey equation (1):

$$\Delta m = -C \frac{\Delta f}{n}$$

Where  $C$  is a constant that depends on the physical properties of the crystal ( $C$ ) ( $17.7\text{ng}\cdot\text{cm}^{-2}\text{Hz}^{-1}$  for the crystal used in this work) and  $n$  is the overtone number (in the following work we will use only the seventh harmonics).

ESR studies were carried out with a Miniscope MS400 (Magnetech, Berlin, Germany) benchtop spectrometer working at X-band with a modulation amplitude of 20 G, a sweep width of 196 G, a sweep time of 30 s, and a microwave power of 10 mW. The temperature was adjusted at  $25^\circ\text{C}$  using a temperature controlled unit TC H03 (Magnetech). All manipulations were performed under air.

### **Synthesis of (1-(1-Phenylethoxy)-2,2,6,6-tetramethylpiperidin-4-ol) (1):**

This synthesis was carried out according to a previously reported procedure<sup>25-26</sup>. Briefly, (1-bromoethyl)benzene (6 mL, 44 mmol) was added to a degassed solution of H-TEMPO (7.9g, 45.8 mmol), copper powder (11.6g, 183 mmol), copper bromide (52.5g, 0.36 mmol) and PMDETA (76.6 $\mu\text{l}$ , 0.36 mmol) in 50 mL of anisole. The reaction mixture was stirred in a sealed tube at  $40^\circ\text{C}$  for 24 h. After filtration, the solution was concentrated under vacuum and purified by column chromatography eluted with hexane/ethyl acetate (95/5 gradually increasing to 50/50) to afford 8.15 g (yield=80%) of a white solid.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 – 7.18 (m, 5H), 4.77 (q,  $J = 6.7$  Hz, 1H), 4.03 – 3.85 (m, 1H), 1.90 – 1.77 (m, 1H), 1.77 – 1.65 (m, 2H), 1.48 (d,  $J = 6.7$  Hz, 3H), 1.33 (s, 3H), 1.23 (s, 3H), 1.07 (s, 3H), 0.66 (s, 3H).

### **Synthesis of (4-acryloyloxy-1-((1'-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (APEOT)) (2) :**

(1) (3 g, 10.8 mmol) and bipyridine (2.54 g, 16.3 mmol) were dissolved in dry dichloromethane (30 mL). The reaction mixture was cooled in an ice-water bath, and a solution of acryloyl chloride (1.31 mL, 16.2 mmol) in dry dichloromethane (10 mL) was slowly added. The mixture was stirred at this temperature for 2 h and then, at room temperature for 24 h. The excess of acryloyl chloride was neutralized with water, and the reaction mixture was then poured into a solution of hydrochloric acid (100 mL, 0.3 M). The organic layer was washed with a solution of sodium hydroxide (100 mL, 0.3 M), dried over magnesium sulfate, and concentrated under vacuum. The product was purified by flash column chromatography using ethyl acetate/hexane as solvent to afford (2) as a light yellow solid (2.67g, 8.04 mmol, yield=75%).  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 (m,  $J = 9.9, 4.7$  Hz, 5H), 6.36 (dd,  $J = 17.2, 1.6$  Hz, 1H), 6.07 (dd,  $J = 17.3, 10.3$  Hz, 1H), 5.79 (dd,  $J = 10.4, 1.5$

Hz, 1H), 5.07 (td, J = 11.4, 5.9 Hz, 1H), 4.78 (q, J = 6.6 Hz, 1H), 1.90 – 1.77 (m, 1H), 1.77 – 1.65 (m, 2H), 1.48 (d, J = 6.7 Hz, 3H), 1.33 (s, 3H), 1.23 (s, 3H), 1.07 (s, 3H), 0.66 (s, 3H).

### **RAFT polymerization of (2): PAPEOT (3)**

Monomer (2) (0.5g, 1.5mmol) was placed in a Schlenk tube under argon. To this, 3ml of a solution of RAFT agent 2-dodecylsulfanylthiocarbonylsulfanyl-2-methyl propionic acid (DMP) (5.5mg, 0.015mmol) and the free radical initiator 2,2'-Azobis (4-methoxy-2,4-dimethylvaleronitrile) V70 (0.7mg, 0.0023mmol) in DMF (3mL), were added. Once the solids were dissolved completely in the solvent, three freeze-pump-thaw cycles were performed. The mixture was stirred at 40°C for various reaction times, and the polymerization was monitored to high conversion. 25ml of MeOH was added and the precipitate was collected, washed with MeOH and dried under reduced pressure overnight. Experimental Mn's were measured by size exclusion chromatography (SEC) against polystyrene (PS) standards and confirmed by <sup>1</sup>H NMR spectroscopy using the end group integration of the chain transfer agent (PAPEOT-CTA) (3).

### **Aminolysis of trithiocarbonate chain end of (3), formation of (4).**

(3) was dissolved in THF and added by an excess of n-butylamine and a catalytic amount of dimethyl phenyl phosphine (DMPP). The reaction occurred for one hour at room temperature under inert atmosphere. A change in color of the solution from yellow to white was observed, and the final product (4) was precipitated in methanol.

### **Oxidation of (4) by thermal treatment to form (5)**

The nitroxide bearing polymer (PTA) was produced by heating a solution of (4) at 135 °C in *tert*-butylbenzene (c = 0.01 g / ml) in the presence of oxygen for 12h. The solvent was then removed under vacuum and the residue was dissolved in a minimum of dichloromethane and precipitated in a mixture of pentane/diethyl ether (1/1 by volume) before drying under vacuum. The redox polymer (5) was recovered as a brown solid.

### **Adsorption of (4) on gold substrate:**

A diluted solution of the (4) (1mg/mL) in THF was drop-casted onto a gold QCM electrode. The sensors were rinsed with THF in order to remove physisorbed molecules and were then dried under a nitrogen stream. The sensor crystal was oscillated and the shift in frequency and

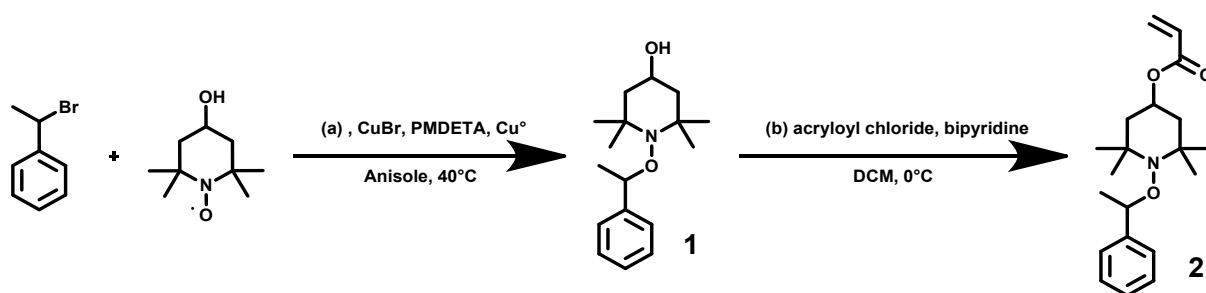
dissipation before and after polymer deposition were noted. The chemisorbed chains were oxidized following the same procedure reported above.

The modified sensor was used as a working electrode to study the redox behavior of the polymer films by using an EQCM unit combined with an AUTOLAB equipped with the potentiostat PGSTAT. The expected capacity was confirmed by performing cyclic voltammetry on the grafted polymer in a 0.5M solution of n-Bu<sub>4</sub>NClO<sub>4</sub> in acetonitrile at a scan rate of 10mVs<sup>-1</sup> and integrating the area under the oxidation peak of a stable CV. All measurements were made at room temperature (20±2 °C).

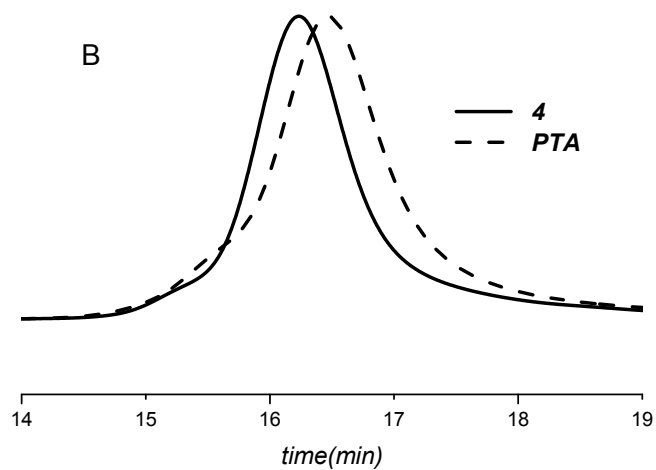
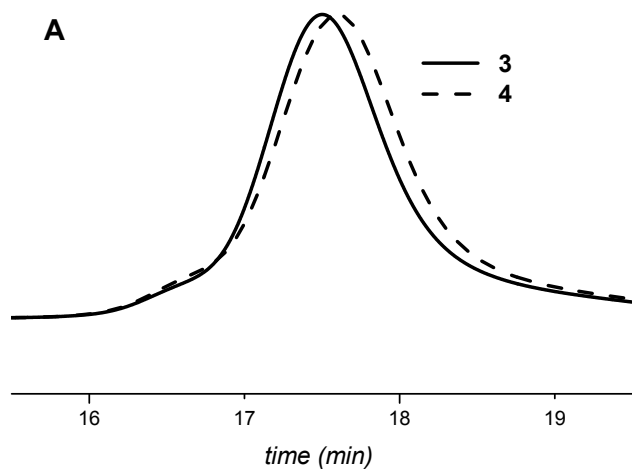
The formula weight-based theoretical redox capacity (in mAh/g):

$$C_{th} = \frac{n N_a e 1000}{M 3600} (mAh/g)$$

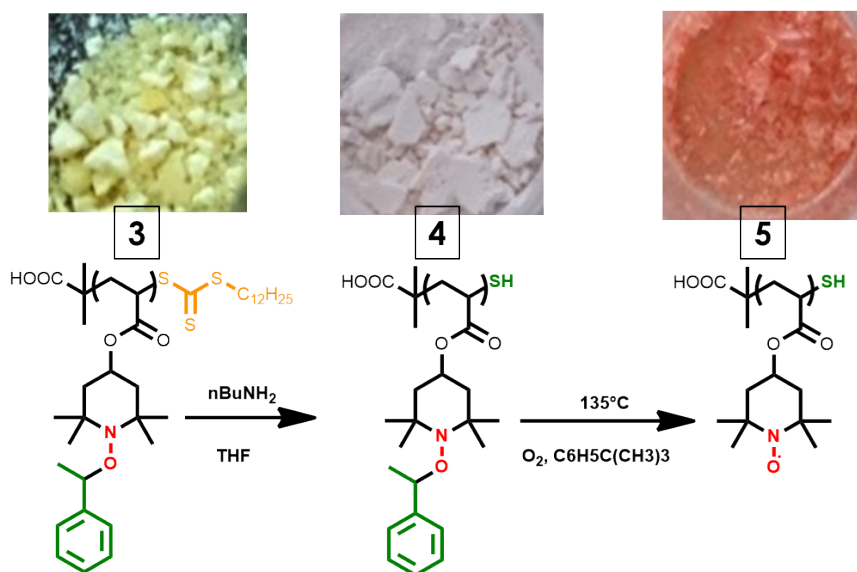
With n, Na, e, and M are stoichiometric number of electrons, Avogadro constant, electric charge for each electron, and the molar mass of the repeating unit respectively.



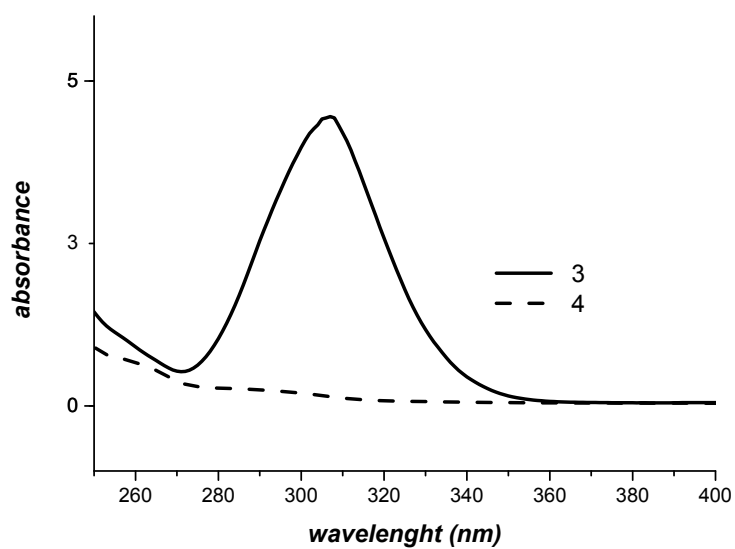
**Scheme S1:** synthesis of acrylate bearing alkoxyamine (**2**).



**Figure S1:** GPC traces of (A) **3** before (solid line) and after aminolysis (product **4**, dash line); (B) **4** before (solid line) and after oxidative thermal activation (dash line).



**Figure S2 :** the aminolysis of chain transfer agents by primary amines and the nitroxides regeneration of the PTA.



**Figure S3:** UV-vis spectra of **3** (solid line) and **4** (dash line) at the concentration of  $1\text{ mg}\cdot\text{mL}^{-1}$  in  $\text{CHCl}_3$

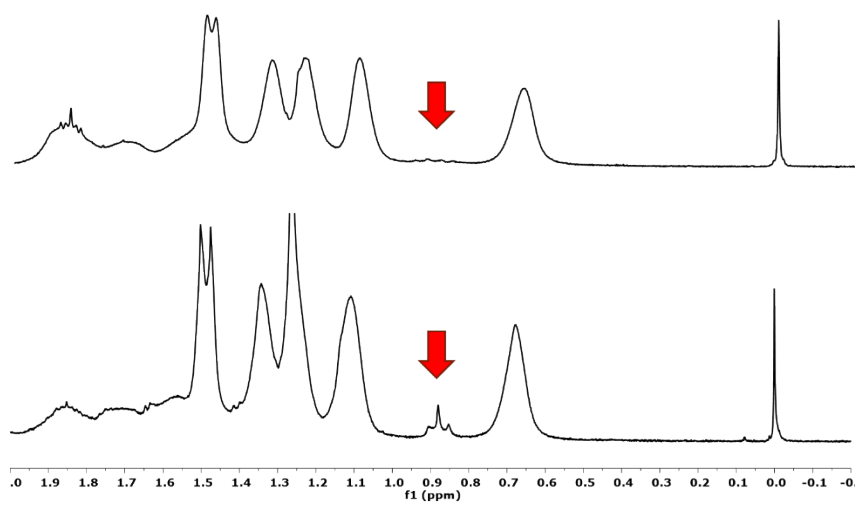
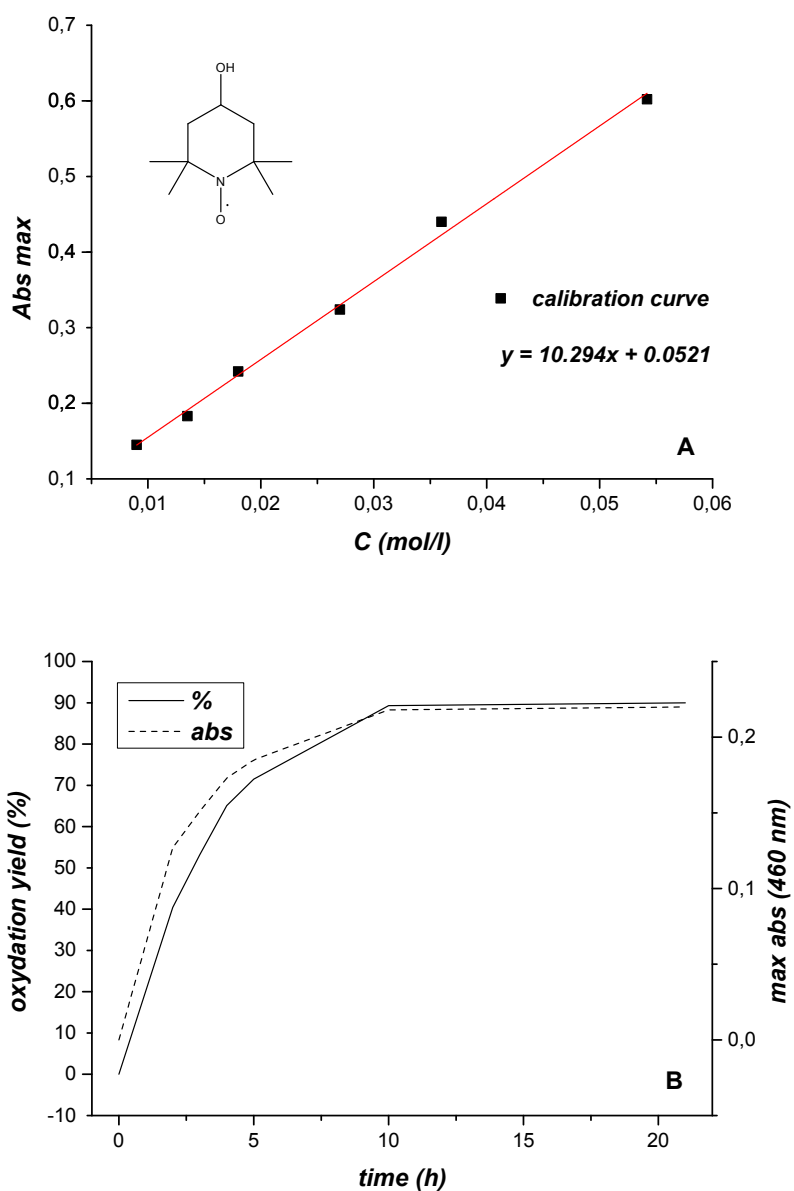
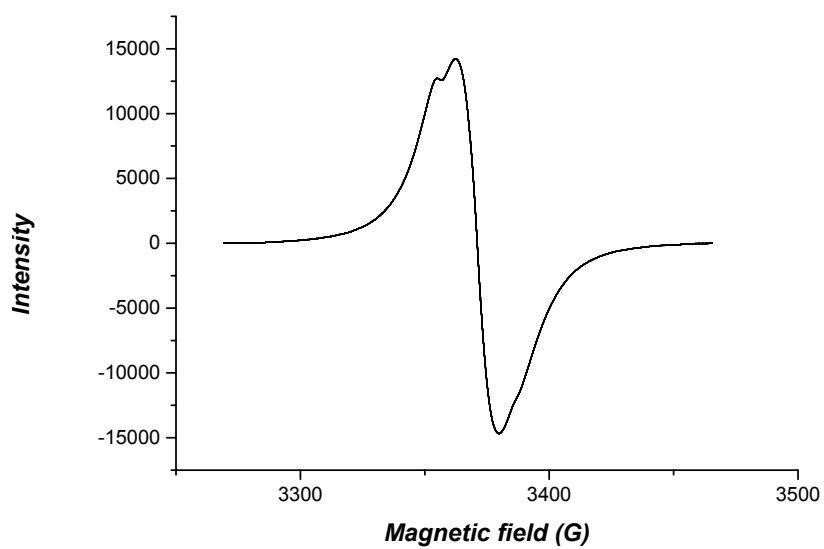


Figure S4: magnification of the  $^1\text{H}$  NMR spectrum of **3** before (below) and after aminolysis (above).

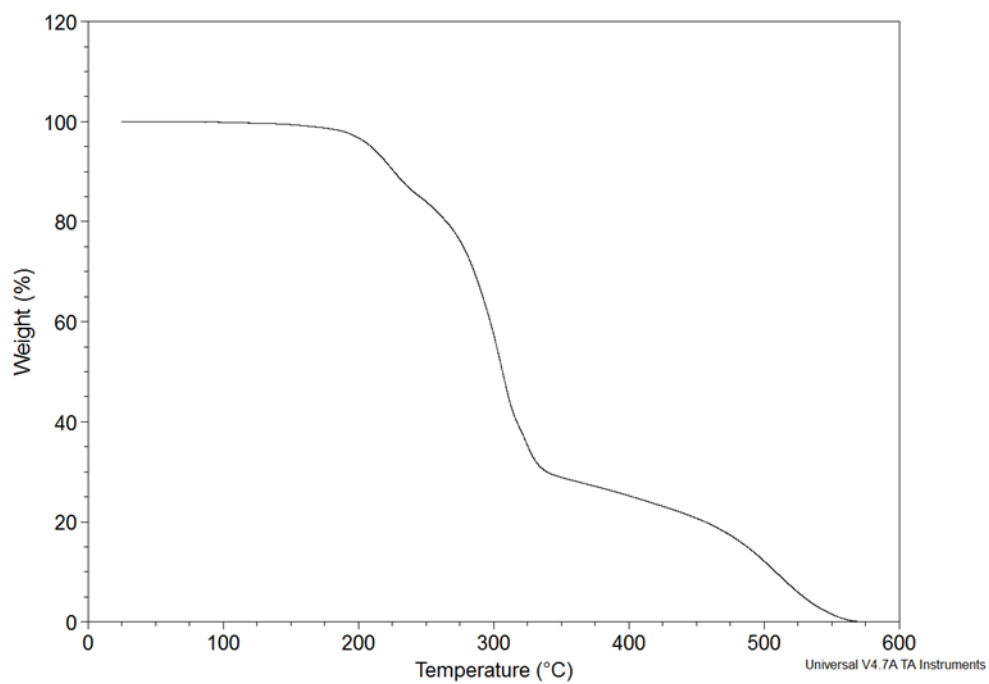




**Figure S5:** (A) Absorbance of different concentration of TEMPO-OH (the chemical structure is inset in the figure) in chloroform. (B) The Oxidation kinetic plot of **4** obtained by monitoring the absorption at 463 nm as a function of time in *tert*-butylbenzene at 135°C under air.



**Figure S6:** ESR spectrum (X-Band) of PTA in *tert*-butyl benzene at room temperature



**Figure S7:** TGA analysis of polyacrylate bearing Tempo under oxygen.