Electronic Supplementary Material (ESI) for Soft Matter.

Chain Shape and Thin Film Behaviour of Poly(thiophene)-*graft*-poly(acrylate urethane)

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Supporting information

Small angle neutron scattering

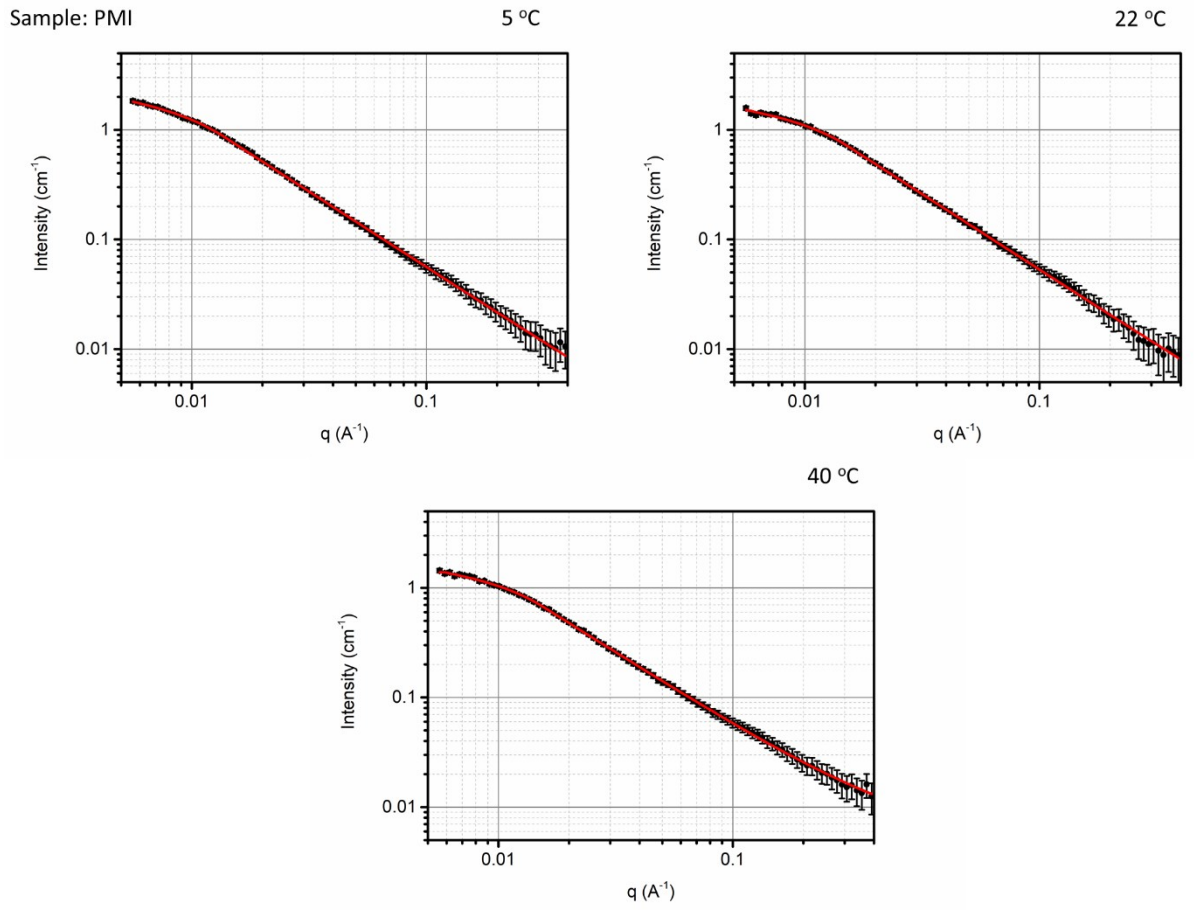

Figure S 1. (black symbol) SANS curves and (red line) Guinier-Porod (GP) model fit for 0.5 wt% **PMI** in THF-d_8 at different temperatures.

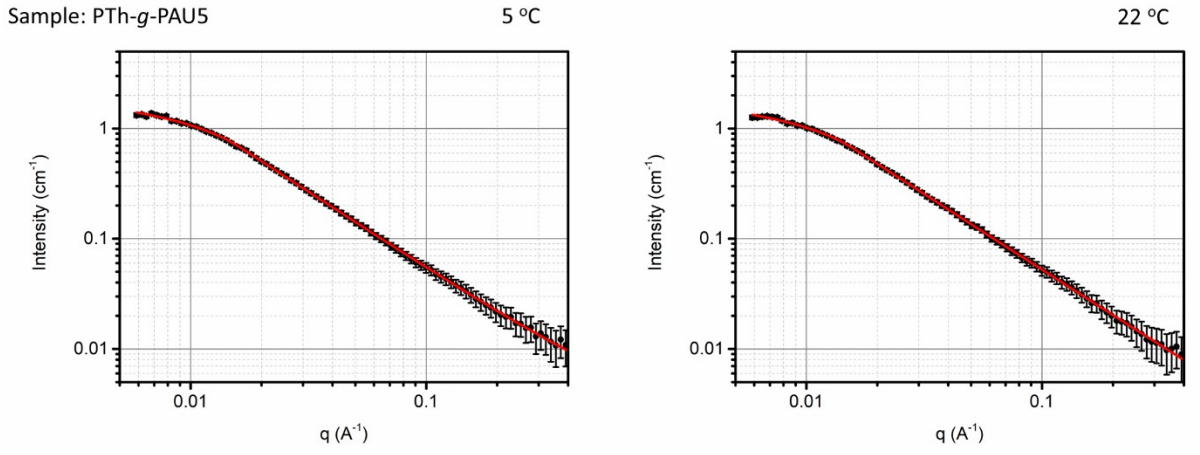

Figure S 2. (black symbol) SANS curves and (red line) GP model fit for 0.5 wt% **PTh-*g*-PAU5** in THF-d_8 at different temperatures.

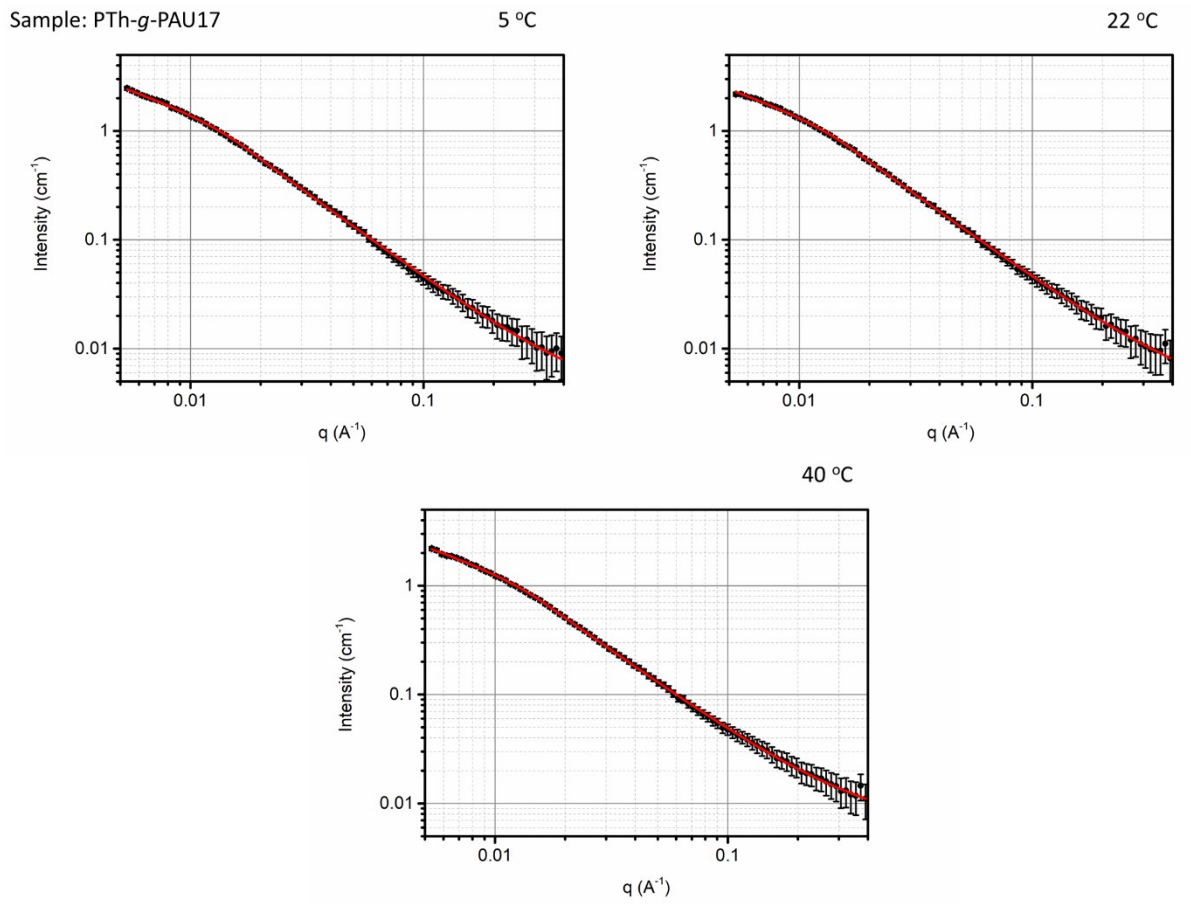

Figure S 3. (black symbol) SANS curves and (red line) GP model fit for 0.5 wt% **PTh-*g*-PAU17** in THF-d_8 at different temperatures.

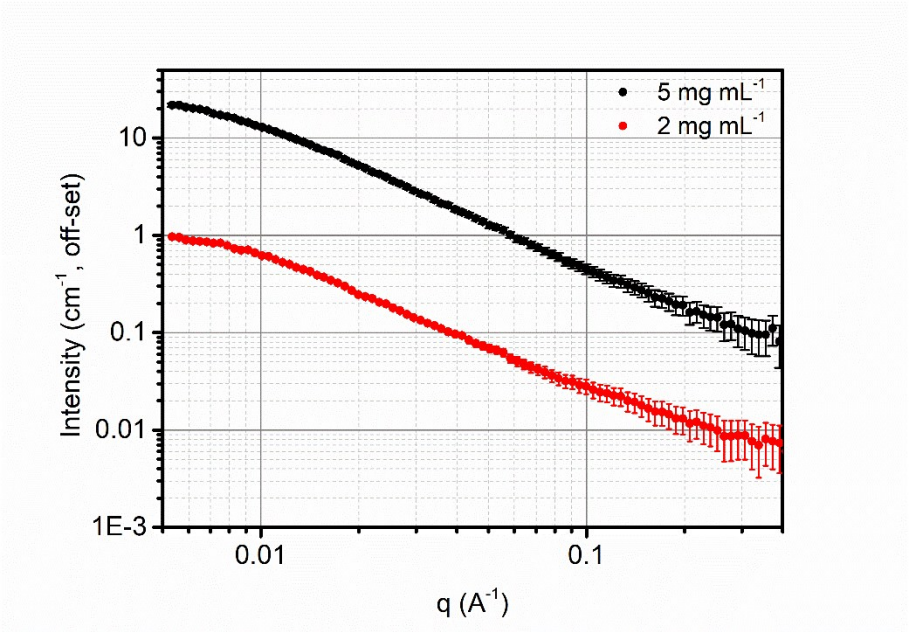

Figure S 4. SANS curves (off-set for clear depiction of individual curves) for **PTh-*g*-PAU17** in THF-d_8 at different concentrations (measured at 22 °C).

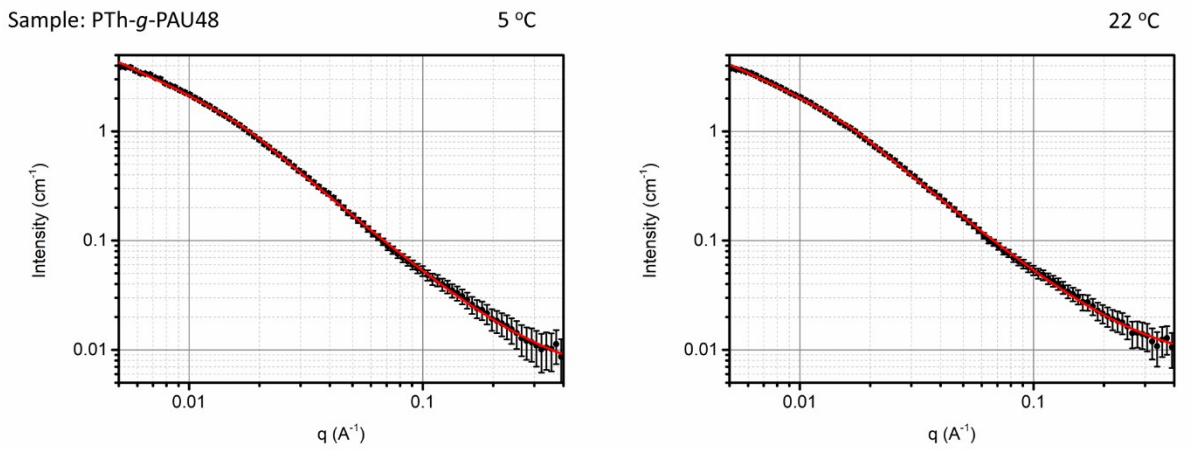

Figure S 5. (black symbol) SANS curves and (red line) GP model fit for 0.5 wt% **PTh-*g*-PAU48** in THF-d_8 at different temperatures.

Table S 1. Summary of conformational properties (Porod exponent, *m*, radius of gyration, R_g, and dimensionality, *S*) of **PTh-*g*-PAU17** in 30:70 vol% $MeOD_4$:THF-d_8 (**Figure 2a**). The SANS curve was fitted using the Guinier-Porod model in two different *q* regions, as indicated in this Table.

Q range	R_g **(Å)**	***S***	***m***
0.003 – 0.03 Å^{-1}	141.1 ± 1.9	1	2.6 ± 0.1
0.02 – 0.4 Å^{-1}	31.2 ± 1.9	0	1.7 ± 0.1

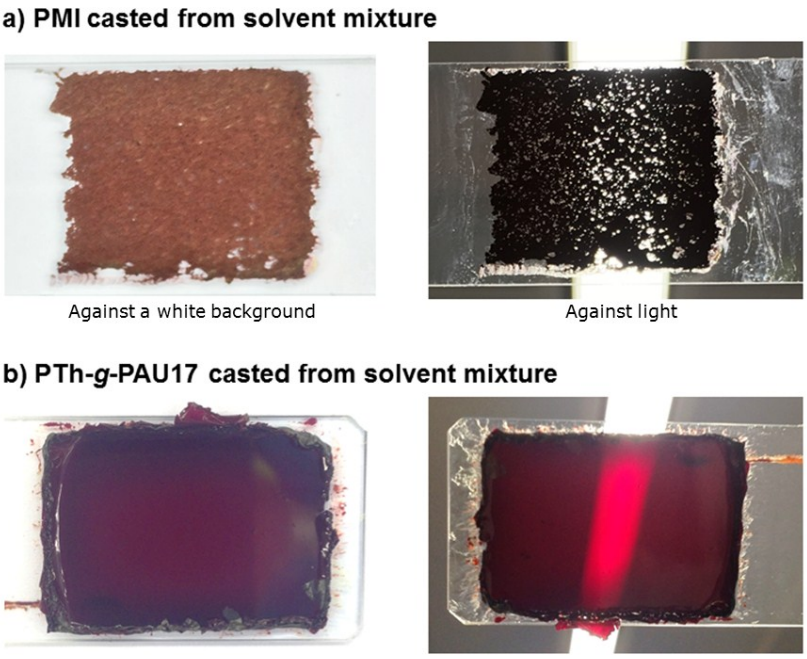

Figure S 6.Optical images of a) **PMI** and b) **PTh-*g*-PAU17** films cast from the solvent mixture.

Electrochemistry

The redox properties and the electron transfer processes of the **PTh-*g*-PAU** thin films were obtained by the means of cyclic voltammetry (CV). CV was carried out for thin drop cast polymer films on Au electrode in the presence of 0.1 M TBAHFP solution in acetonitrile. Despite having low **PTh** content in all graft copolymers (33, 26 and 20 wt% in **PTh-*g*-PAU5**, **PTh-*g*-PAU17**, and **PTh-*g*-PAU48**, respectively), CVs presented in **Figure S7** showed excellent electroactivity, comparable to the ungrafted macroinitiator. The plot of linear dependence of anodic and cathodic peak current on the square root of scan rate (**Figure S 8**) for all polymers showed excellent fits to a linear relationship with R^2 value close to 1, indicating a diffusion-controlled process for all of the polymers.

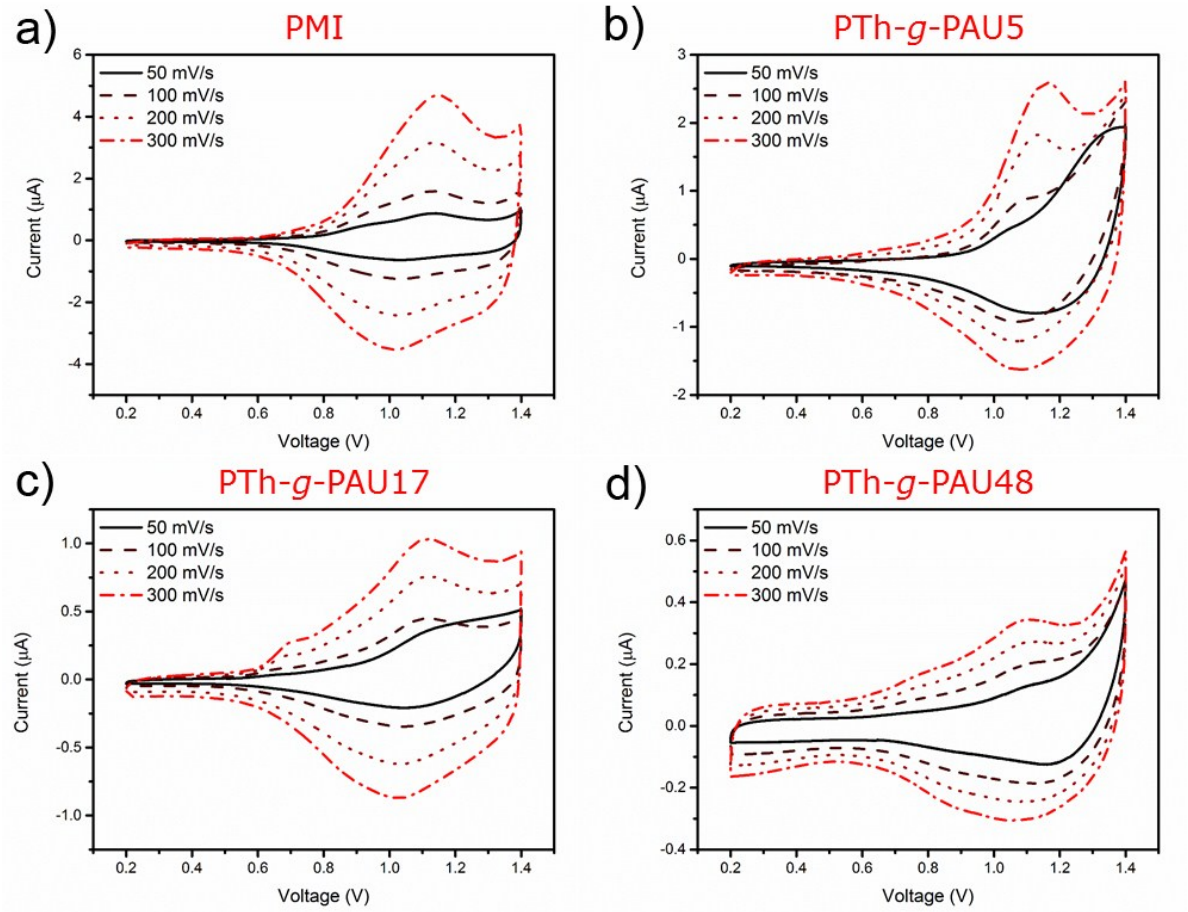

Figure S 7. a-d) CVs of the polymers obtained at different scan rates in 0.1 M TBAHFP/acetonitrile solution. 0.15 wt% polymer solution in THF was drop cast onto 1 mm diameter Au electrode with leak-free, poly(ether ether ketone)-based electrode as reference and Pt wire as counter electrodes.

Table S 2. Redox peak potentials of polymers obtained from CVs performed at 100 mV s^{-1} (**Figure S 7**).

@ 100 mV s^{-1}	$E_{oxidation}$ (V)	$E_{reduction}$ (V)
PMI	1.13	1.03
PTh-*g*-PAU5	1.09	1.07
PTh-*g*-PAU17	1.12	1.05
PTh-*g*-PAU48	1.12	1.13

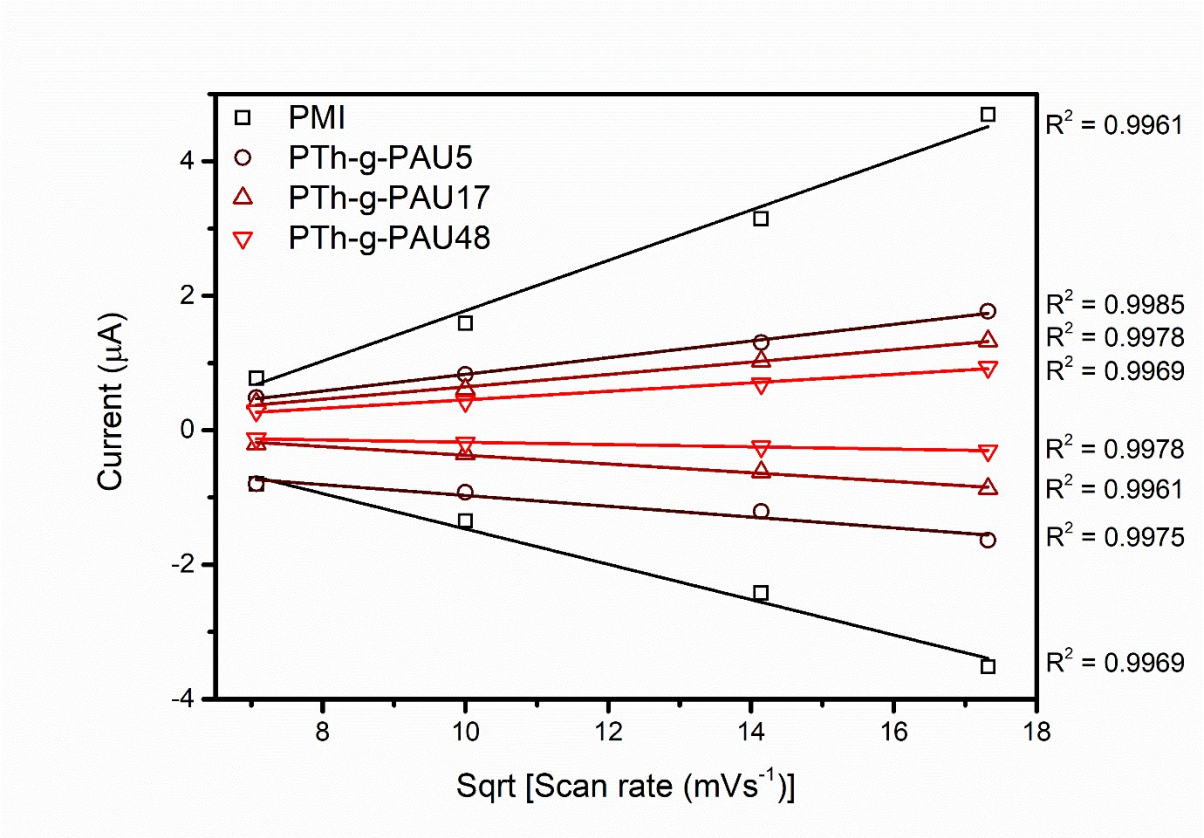

Figure S 8. Plots of anodic and cathodic peak currents versus square root of the scan rates obtained from CV measurements (**Figure S 7**) for all polymers.

In situ electrochemical neutron reflectivity

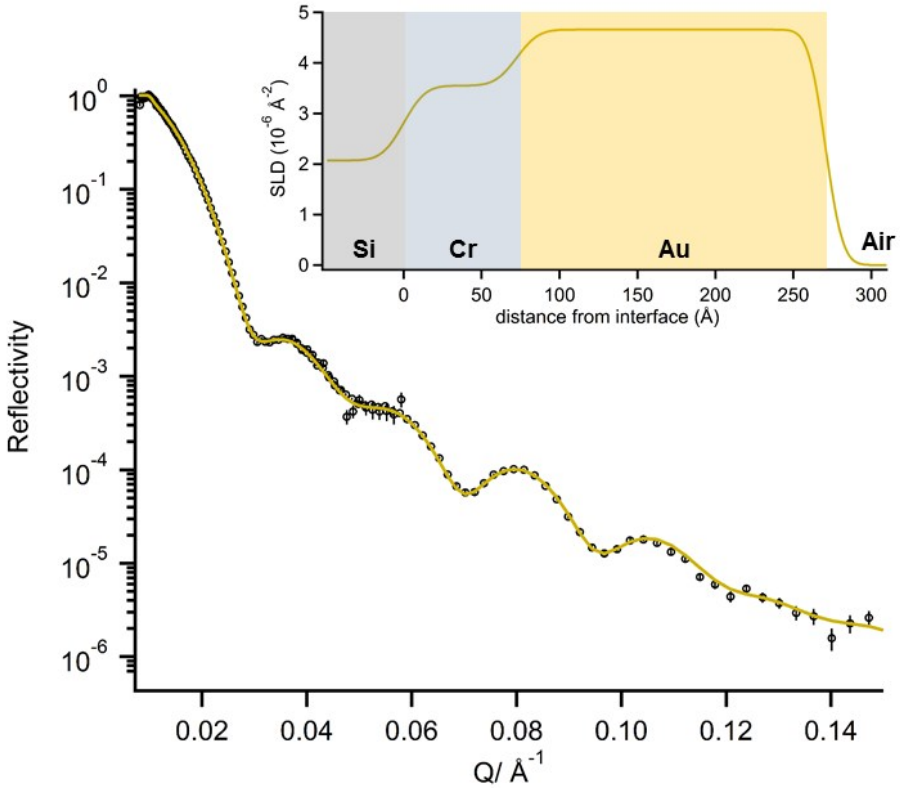

Figure S 9. NR profile of bare Au/Cr electrode. The solid line represents the best fit to the data. Inset: neutron scattering length density (nSLD) profile of the Au/Cr electrode.

Table S 3. Summary of parameters obtained from fitting NR data of bare Au/Cr electrode (**Figure S 9**).

	Thickness (Å)	**nSLD (10^{-6} Å^{-2})**	**nSLD$_{theoretical}$ (10^{-6} Å^{-2})**	**Roughness (Å)**
Si	-	2.07	2.07	11 (0.1)
Cr	75 (0.5)	3.55	3.03	11 (0.1)
Au	198 (0.4)	4.66	4.66	15 (0.1)

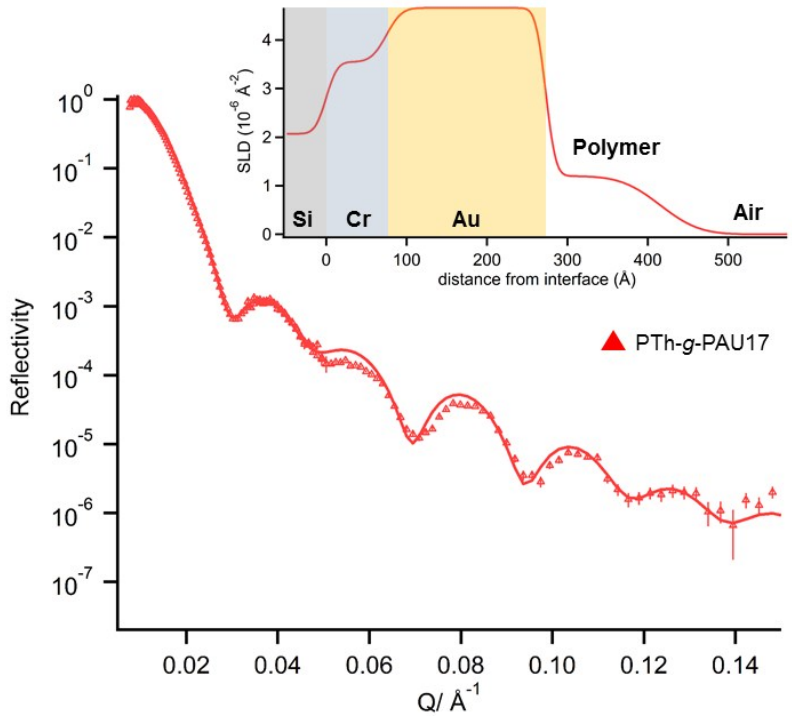

Figure S 10. NR profile of **PTh-*g*-PAU17** thin film on Au/Cr electrode measured in air. The thin film was prepared for *in situ* electrochemical NR measurement. The solid line represents the best fit to the data. Inset: neutron scattering length density (nSLD) profile of the thin film on Au/Cr electrode.

Table S 4. Summary of parameters obtained from fitting NR data (**Figure S 10**) of **PTh-*g*-PAU17** thin film on Au/Cr electrode. The thin film was prepared for *in situ* electrochemical NR measurement.

	Thickness (Å)	**nSLD (10^{-6} Å^{-2})**	**Roughness (Å)**
Si	-	2.07	11
Cr	75	3.55	11
Au	198	4.66	15
PTh-*g*-PAU17	143 (6)	1.20	38 (5)

Comment [AS]: I would be very concern about this fit. I am not a specialist in the reflectivity, but just looking at it here I would like to have an explanation here why last four peaks on the fit are consistently shifted to the lower Q, comparing to the original data.
In other words – there is something systematic, at least by eye, and it needs explanation.

Comment [PB]: Hi Anna, I have discussed this with Andrew and his comment was that this is the best fit of the data using a single layer in the model. The shift could be due to uneven coverage of the film on the surface but Andrew said it is the best we can get. A more complex model can be tried but he believes it would be too complex with nothing more gained from this.

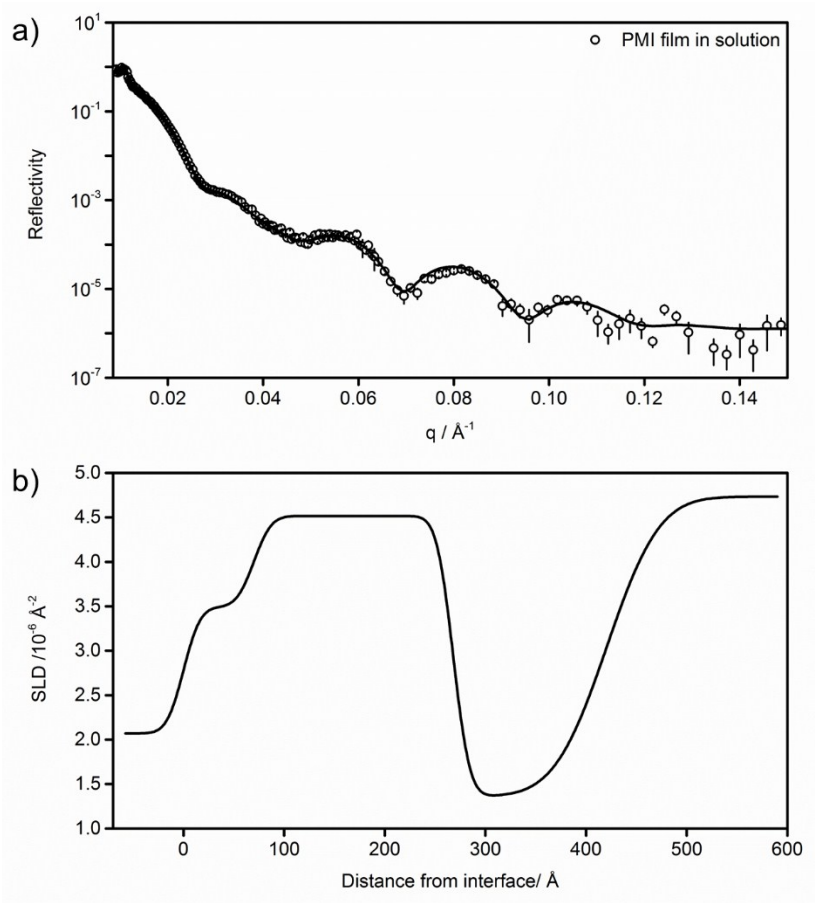

Figure S 11. a) NR profile of macroinitiator, **PMI** and b) corresponding nSLD profile in 0.1 M TBAHFP/acetonitrile-d_3 solution.

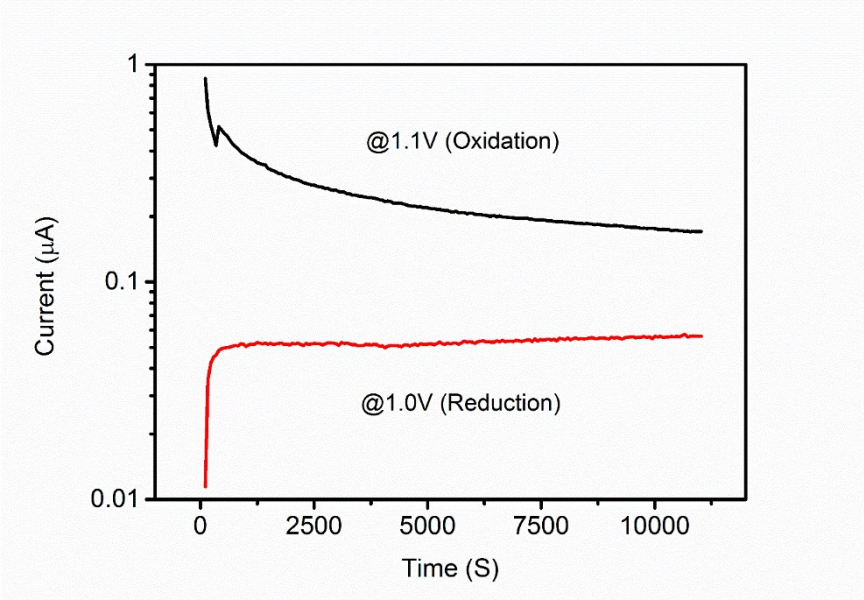

Figure S 12. Chronoamperometric response of **PTh-*g*-PAU17** thin film on Au/Cr electrode held at constant potentials of +1.1 or +1.0 V during NR measurement. Chronoamperometry was conducted in 0.1 M TBAHFP/acetonitrile-d_3 A bare Au/Cr electrode was used as the counter electrode.