Electronic Supplementary Information (ESI)

Polynitroxide copolymers to reduce biofilm fouling on surfaces

Nathan R.B. Boase,[a] Marcelo D.T. Torres,[b,c,d] Nicholas L. Fletcher,[e,f] Cesar de la Fuente-Nunez,[b,c] and Kathryn E. Fairfull-Smith*[a]

[a]*School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology (QUT), 2 George St, Brisbane, Australia.*
[b]*Synthetic Biology Group, MIT Synthetic Biology Center, Department of Biological Engineering and Electrical Engineering & Computer Science, Research Laboratory of Electronics, Massachusetts Institute of Technology, 77 Massachusetts Ave, Cambridge, MA, USA.*
[c]*Broad Institute of Massachusetts Institute of Technology and Harvard, 415 Main St, Cambridge, MA, USA.*
[d]*Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, 5001 Avenida dos Estados, Santo Andre, SP, Brazil.*
[e]*Centre for Advanced Imaging, University of Queensland, St Lucia, Queensland 4072, Australia*
[f]*Australian Institute for Bioengineering and Nanotechnology, ARC Centre of Excellence in Convergent Bio-Nano Science and Technology, University of Queensland, St. Lucia, Queensland 4072, Australia*

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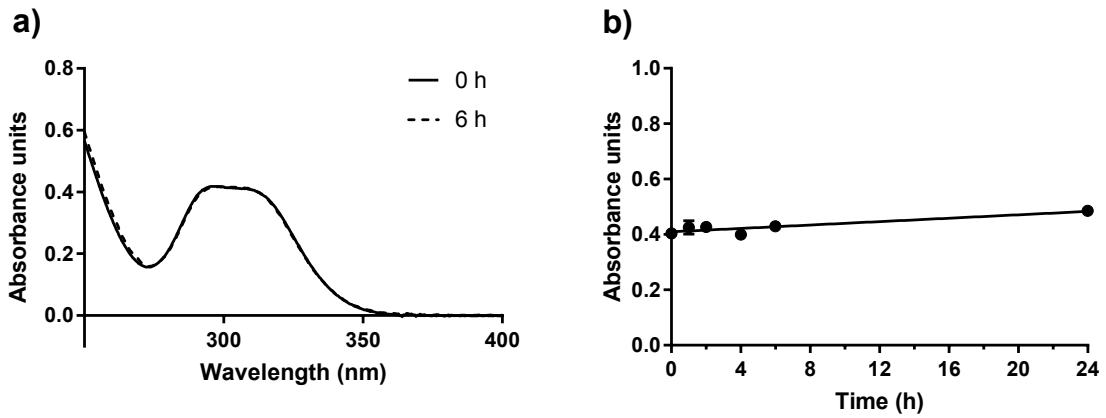

Figure 1: Model reaction determining stability of trithiocarbonate RAFT agent to aminolysis by TMPM monomer. (a) UV-Vis absorbance spectrum of model reaction (100 TMPM:1 CPPTTC, dioxane) at 85°C at 0 and 6 h, (b) Absorbance of trithiocarbonate RAFT agent from model reaction at 308 nm, showing stability over time (each time point average of two measurements).

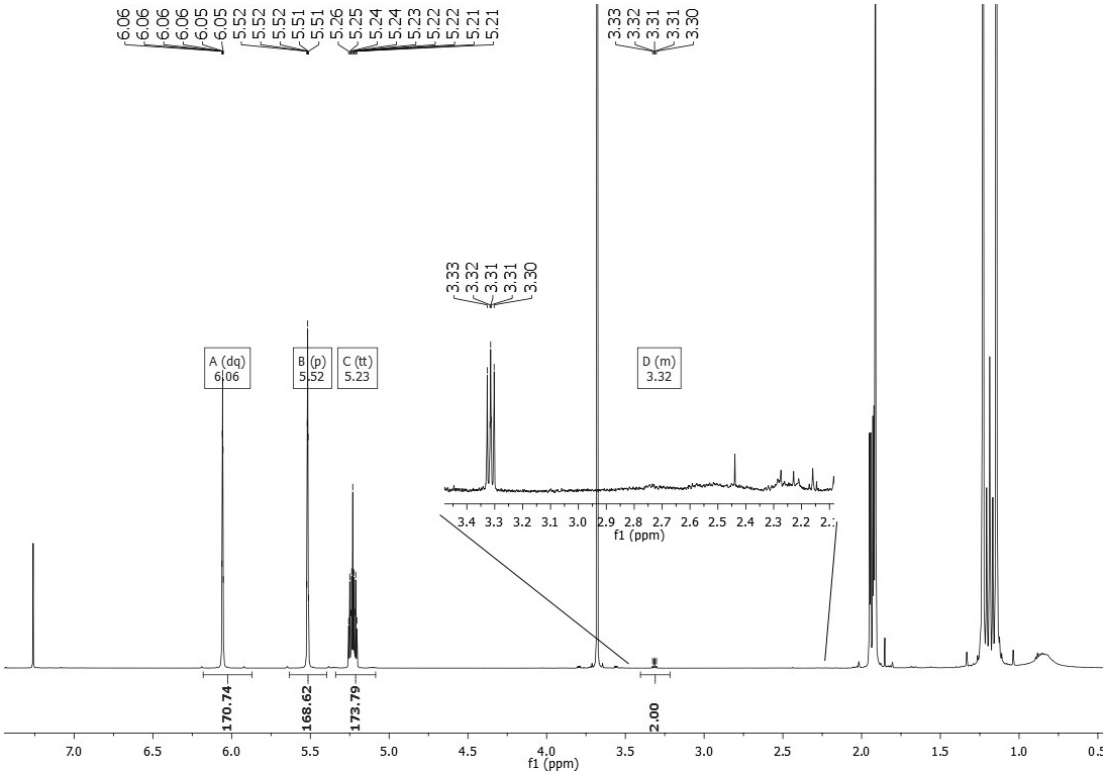

Figure 2: ^{1}H NMR spectrum of a mixture of TMPM and CPPTTC at polymerisation concentrations and heated at 85 °C in dioxane for 5 hours. Peak D represents the α-methylene of the Z-group of the RAFT agent and show's no evidence of aminolysis to form any free pentane thiol.

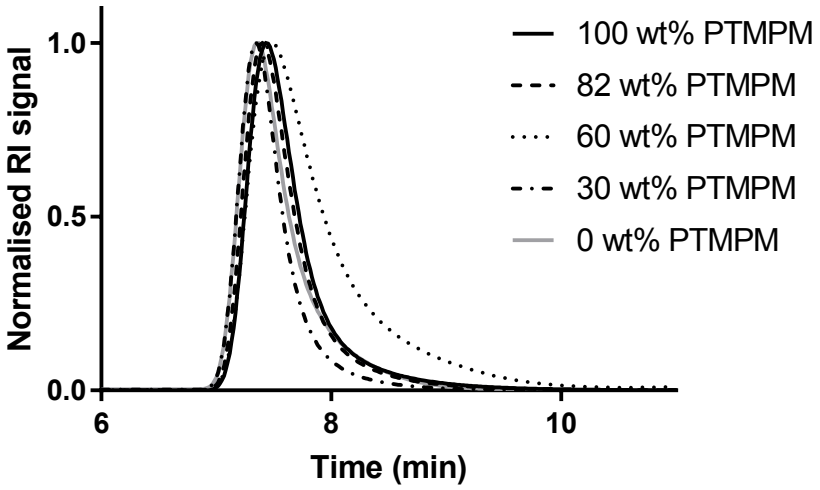

Figure 3. Normalised SEC traces of PTMPM-PMMA copolymers synthesised in this study. SEC was run at 60 °C with DMAc with 1% LiBr was used as eluent.

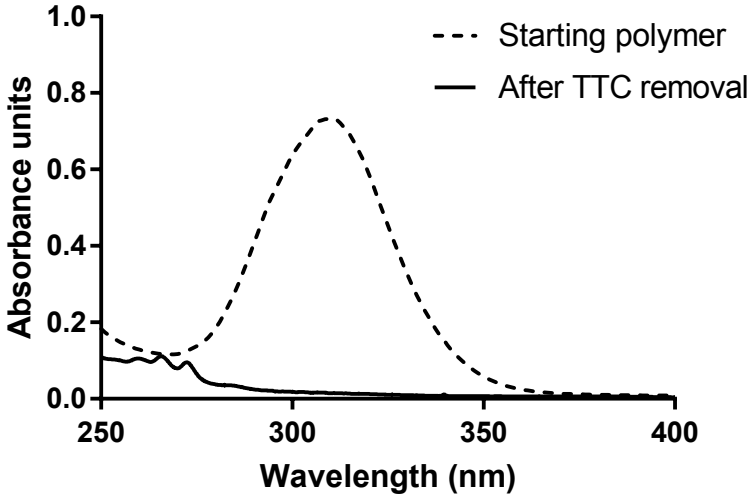

Figure 4: UV-Vis characterisation of the removal of trithiocarbonate groups from the polymers by oxidation, as evidenced by characteristic loss of thiocarbonylthio peak at 308 nm.

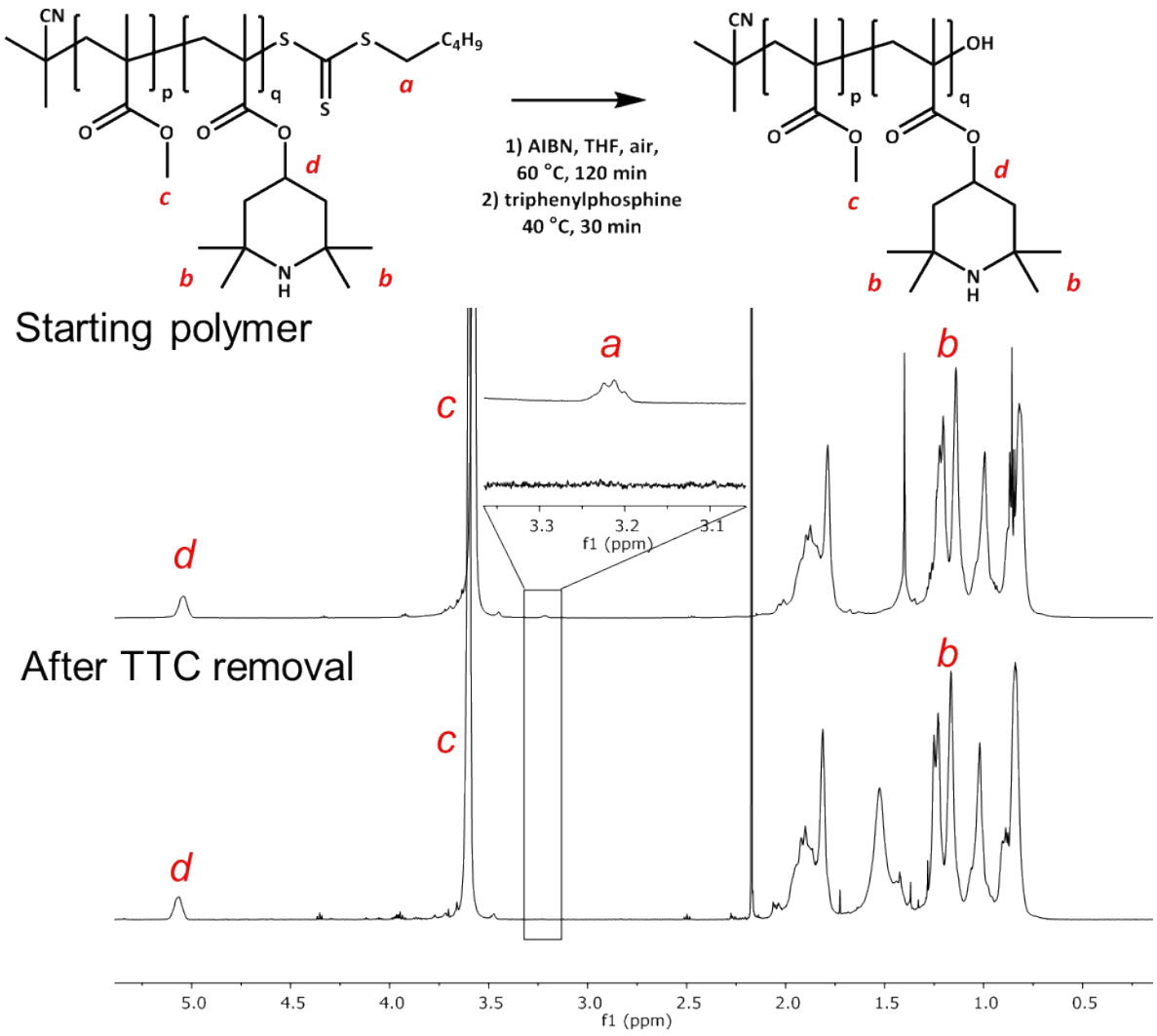

Figure 5: ^{1}H NMR spectroscopic characterisation of the removal of trithiocarbonate groups from the polymers by oxidation, as evidenced by characteristic loss of α-methylene of the Z-group of the RAFT agent.

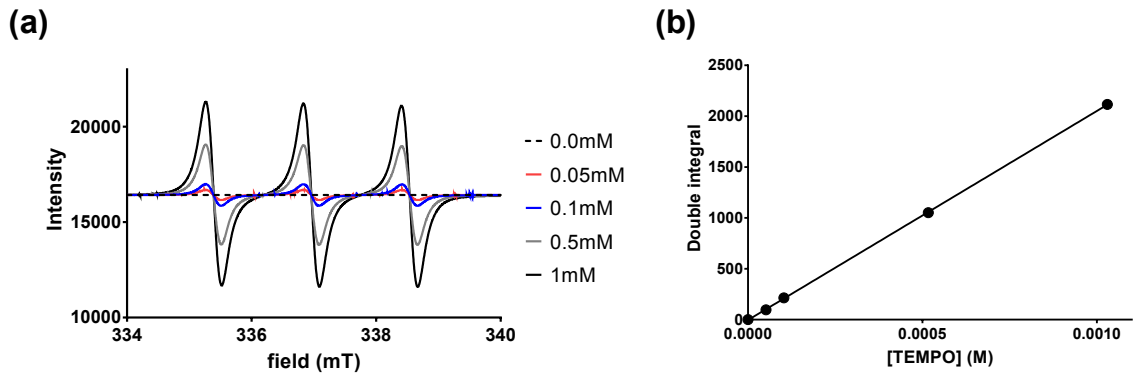

Figure 6: EPR spectroscopy standard curve of TEMPO used to quantify nitroxide concentration in polymers. (a) EPR spectra of TEMPO from 0 – 1 mM, (b) standard curve of the double integral of the EPR spectra in (a). Slope = 2100000 M^{-1} (r^2 = 0.9999).

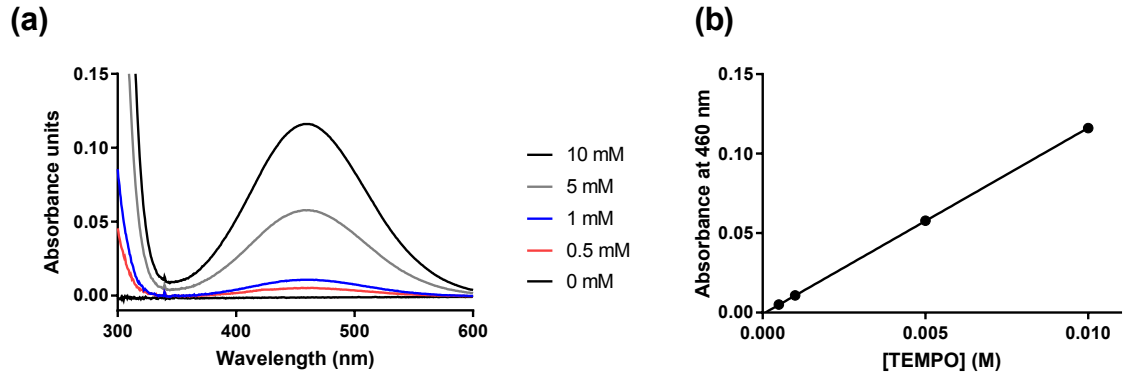

Figure 7: UV-Vis standard curve of TEMPO used to quantify nitroxide concentration in polymers. (a) UV-Vis spectra of TEMPO from 0 – 10 mM, (b) standard curve of max absorbance at 460 nm. E= 11.72 $M^{-1}.cm^{-1}$ (r^2 = 1).

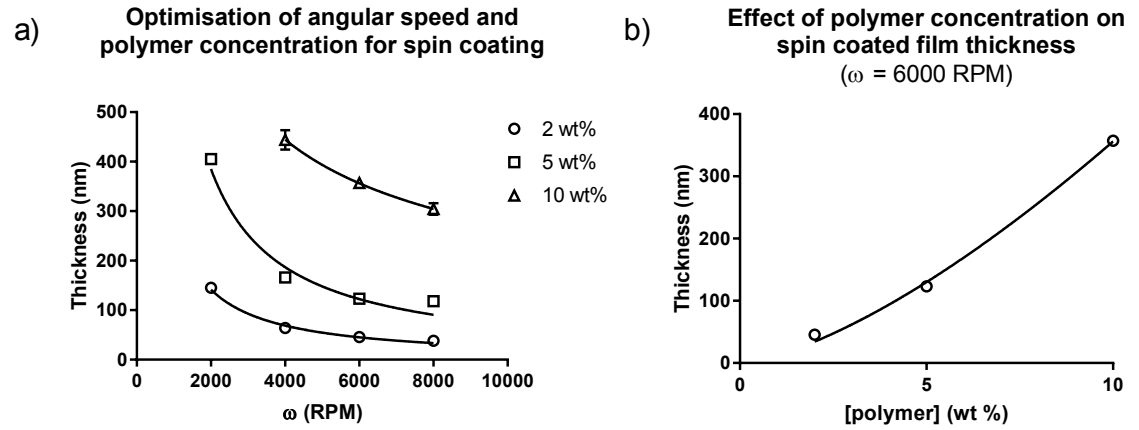

Figure 8: Optimisation of spin coating conditions, for (a) spin conditions and (b) concentration, using 100 wt% PMMA in toluene.

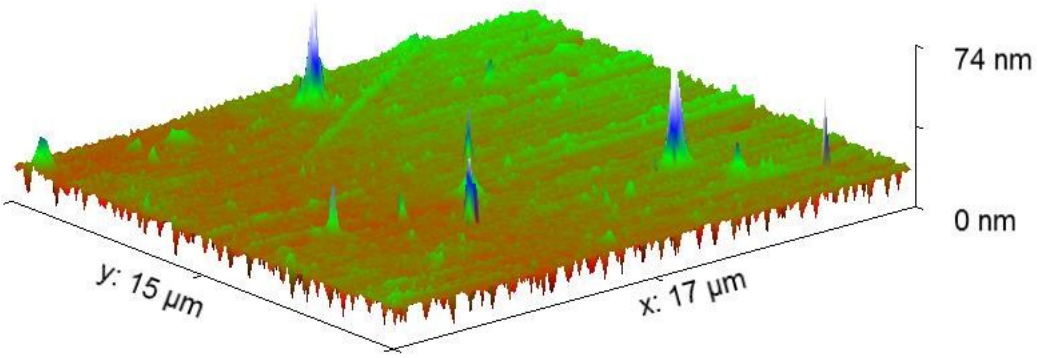

Figure 9: 3D view of AFM measurement of 100% PMMA film, spin coated onto silicon wafer demonstrating that the surface is smooth without features. RMS roughness of entire FOV ± 3.0 nm (255 µm^2). Some dust particles are evident on the surface as the narrow and intense peaks approximately 70 nm high.

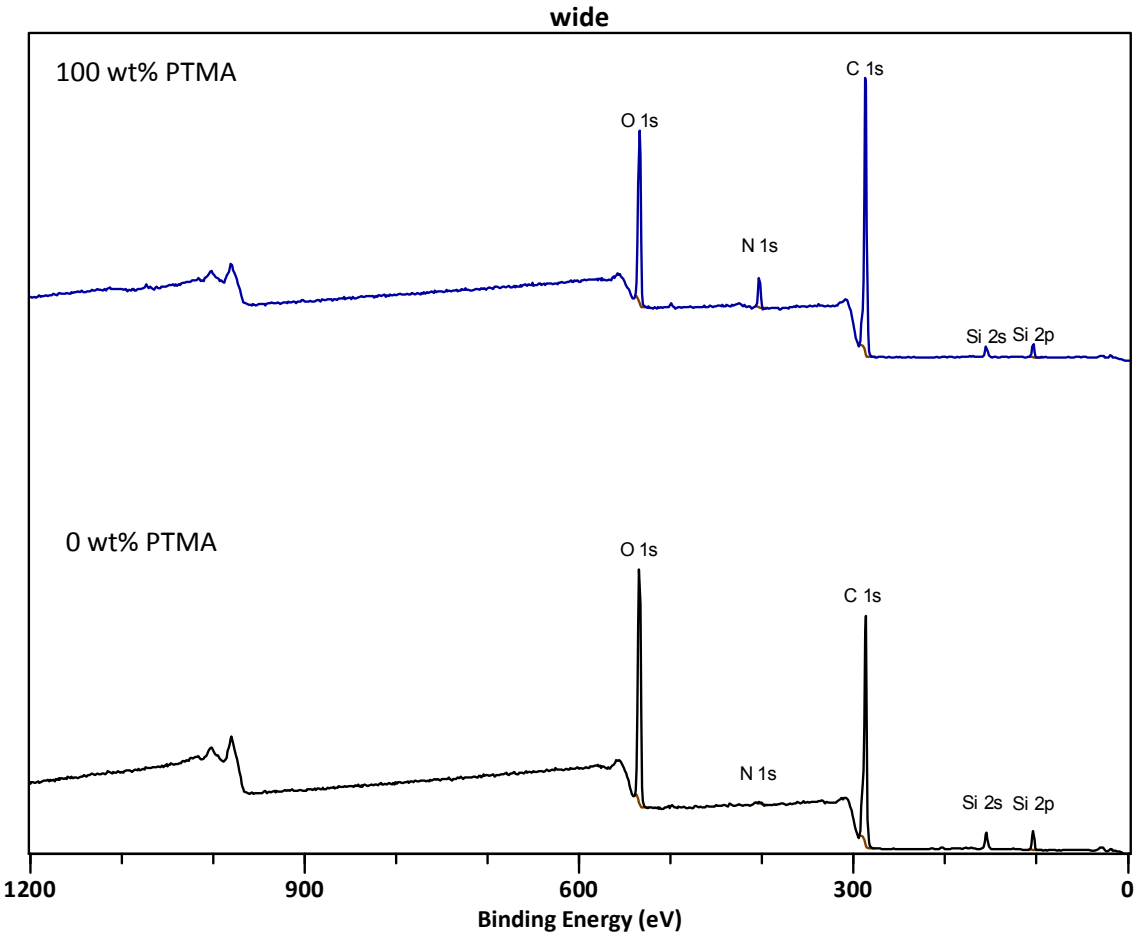

Figure 10: XPS survey spectrum of 100 wt% PTMA and 0 wt% PTMA films.

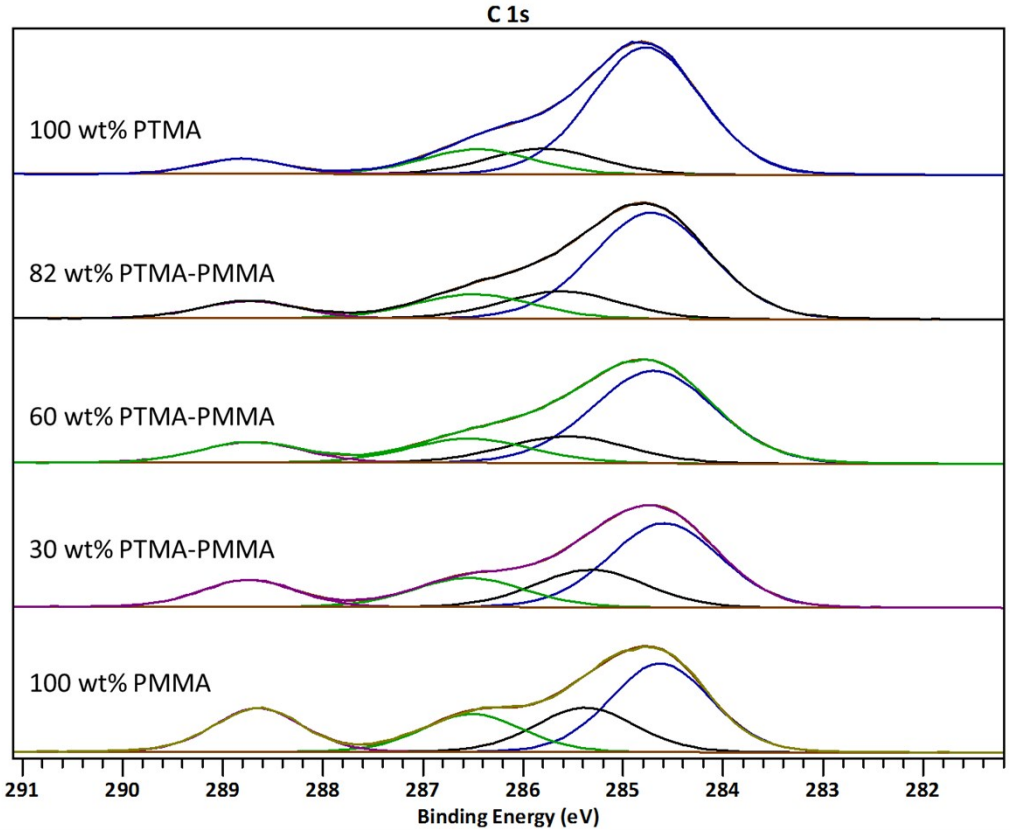

Figure 11: High resolution XPS spectra of the C1s region for each of the PTMA-PMMA copolymers.

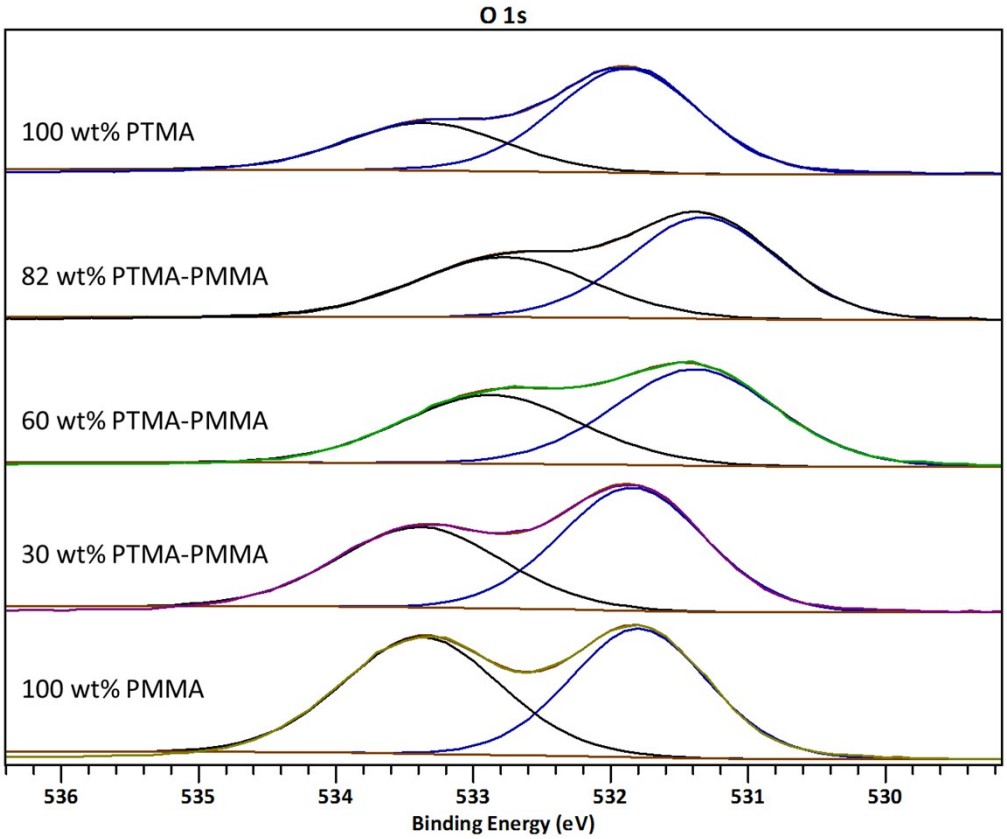

Figure 12: High resolution XPS spectra of the C1s region for each of the PTMA-PMMA copolymers.

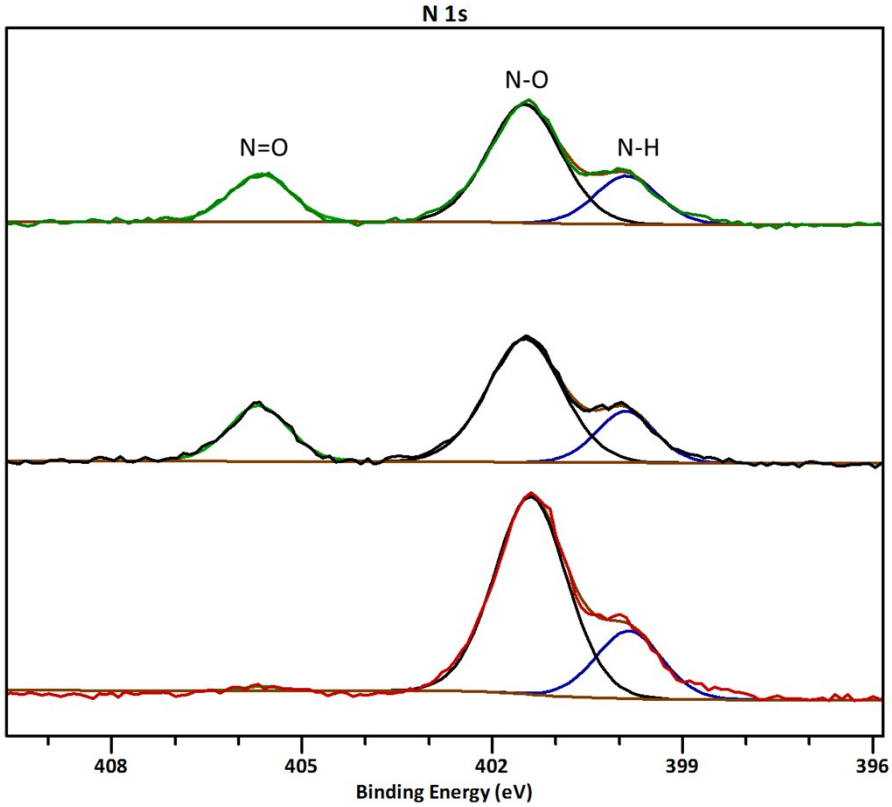

Figure 13: Replicate high resolution XPS N1s spectra acquired for the same 100 wt% PTMA film, at three different locations, demonstrating the variability of the peak at 406 eV.

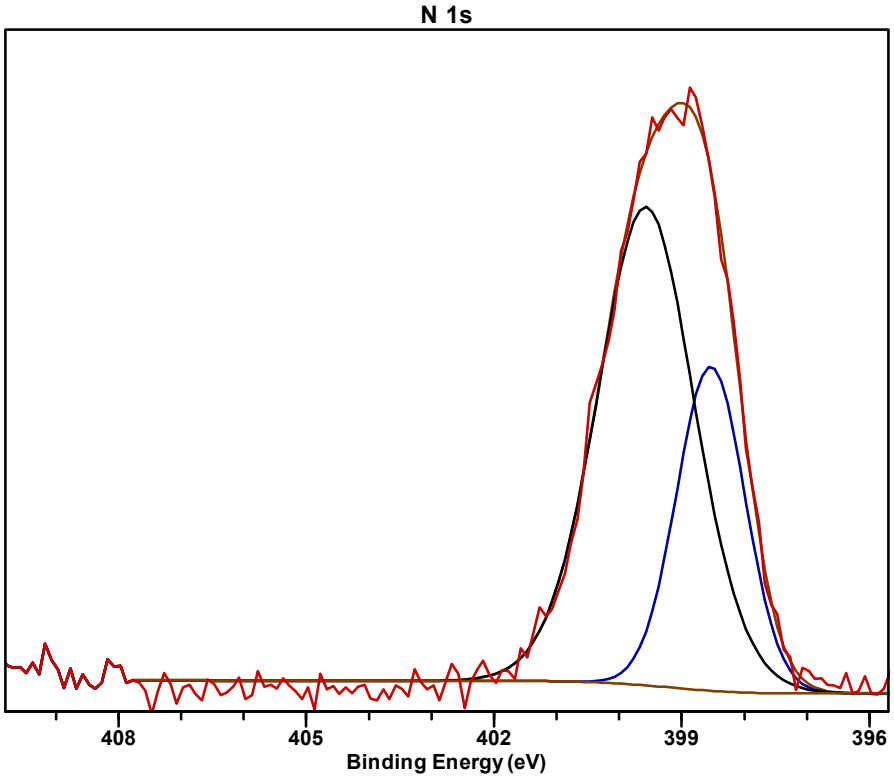

Figure 14: High resolution XPS N1s spectrum of neat PTMA powder, showing that there is no peak at 306 eV for the oxoammonium cation.

Table 1: Summary statistics for two-way ANOVA analysis of anti-biofilm activity of nitroxide copolymer surfaces.

ANOVA summary	
F	13.64
P value	<0.0001
P value summary	****
Significant diff. among means (P < 0.05)?	Yes
R square	0.7912

ANOVA table	**SS**	**DF**	**MS**	**F (DFn, DFd)**	**P value**
Treatment (between columns)	50.51	5	10.1	F (5, 18) = 13.64	P<0.0001
Residual (within columns)	13.33	18	0.7406		
Total	63.84	23			

Dunnett's multiple comparisons test	**Mean Diff.**	**95.00% CI of diff.**	**Summary**	**Adjusted P Value**	**% reduction in attached bacteria**
0 wt% PTMA-PMMA vs. 30 wt% PTMA-PMMA	2.58	0.8991 to 4.26	**	0.0021	99.69
0 wt% PTMA-PMMA vs. 60 wt% PTMA-PMMA	2.47	0.7894 to 4.15	**	0.0032	99.69
0 wt% PTMA-PMMA vs. 82 wt% PTMA-PMMA	3.122	1.442 to 4.802	***	0.0003	99.91
0 wt% PTMA-PMMA vs. 100 wt% PTMA	4.115	2.435 to 5.796	****	0.0001	99.96