Supporting Information

Investigating the Adsorption of Anisotropic Diblock Copolymer Worms onto Planar Silica and Nanocellulose Surfaces using a Quartz Crystal Microbalance

Joakim Engström,^a‡ Michael S. Reid,^b Emma E. Brotherton,^c Eva Malmström,^a Steven P. Armes,^c Fiona L. Hatton*^c†

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

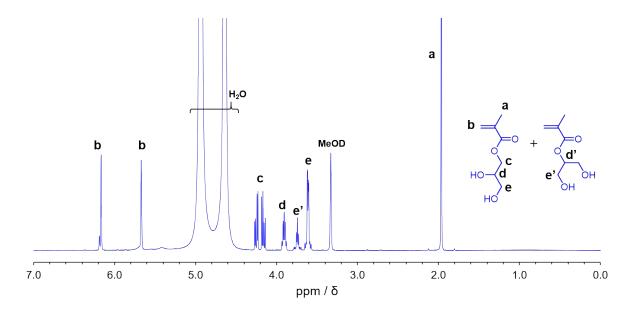


Figure S1. ¹H NMR (400 MHz, CD₃OD) spectrum obtained for glycerol monomethacrylate (GMA) prepared by hydrolysis of glycidyl methacrylate (GlyMA).

^a. Division of Coating Technology and Wallenberg Wood Science Center, School of Engineering Sciences in Chemistry, Biotechnology and Health, Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

b. Division of Fibre Technology, School of Engineering Sciences in Chemistry, Biotechnology and Health, Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

^c Dainton Building, Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, South Yorkshire, S3 7HF, UK

[†] Present address: Department of Materials, Loughborough University, Loughborough, LE11 3TU, UK.

[‡] Present address: Departments of Bioengineering and Materials Science and Engineering, University of California, Berkeley, 210 Hearst Mining Building, Berkeley, CA 94720, USA

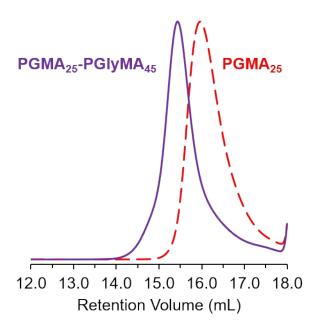


Figure S2. Overlaid DMF GPC chromatograms recorded for the PGMA₂₅ homopolymer precursor and the PGMA₄₅-PGlyMA₂₅ diblock copolymer prepared at 15% w/w solids by RAFT aqueous emulsion polymerization of GlyMA.

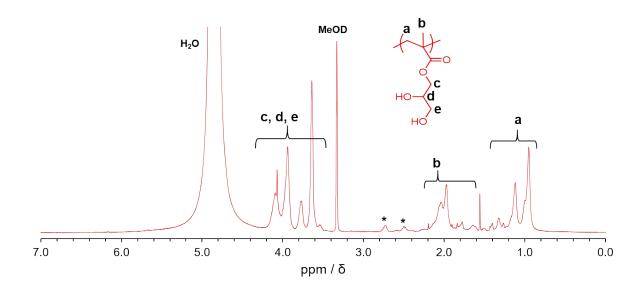


Figure S3. ¹H NMR (400 MHz, CD₃OD) spectrum recorded for the PGMA₂₅ precursor. The reaction mixture was sampled after the RAFT aqueous solution polymerization of GMA for 3 h and diluted with CD₃OD. Asterisks (*) indicate peaks arising from chain-ends originating from use of the CECPA RAFT agent; the signal at 2.73 ppm corresponds to two CH₂ protons (HOOC-C \underline{H}_2 -CH₂-S-C(=S)-S-), while the signal at 2.50 ppm corresponds to four CH₂ protons (-C(CN)(CH₃)-C \underline{H}_2 -COOH).

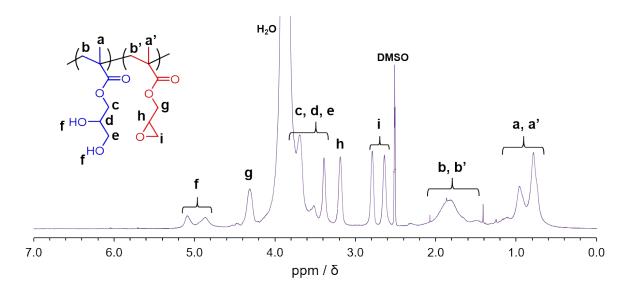


Figure S4. ¹H NMR (400 MHz, d_6 -DMSO) spectrum recorded for the PGMA₂₅-PGlyMA₄₅ diblock copolymer prepared by RAFT aqueous emulsion polymerization of GlyMA. An aliquot from the final reaction mixture was diluted with d_6 -DMSO.

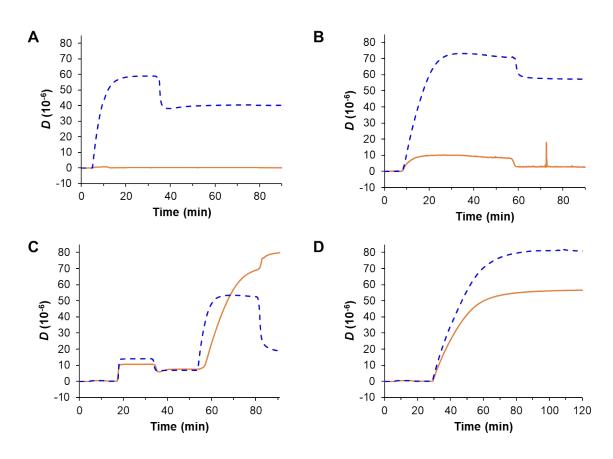


Figure S5. QCM-D dissipation (*D*) monitoring at a flow rate of 0.15 mL min⁻¹ during adsorption of 0.1 g dm⁻³ aqueous dispersions of either anionic PGMA₂₅-PGlyMA₄₅ worms (orange solid lines) or cationic crosslinked PGMA₂₅-P(GlyMA_{-EDA})₄₅ worms (blue dashed lines) on the following surfaces: (A) silica, (B) CNCs, (C) CNFs and (D) PEI-coated silica.

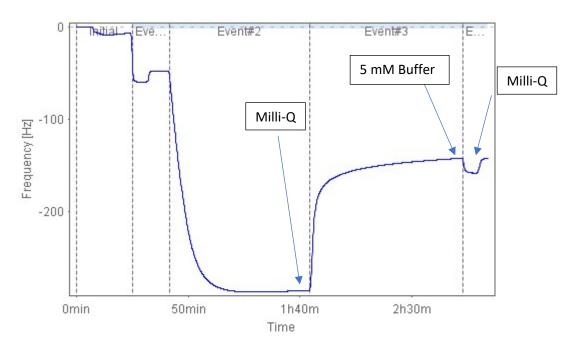


Figure S6. QCM-D analysis of the adsorption of cationic cross-linked PGMA₂₅-P(Gly-EDA)₄₅ worms onto an *in situ* generated CNF surface. The introduction of buffer, as marked after the rinsing step using Milli-Q water, is shown to indicate the effect of counter-ion exchange on the frequency shift ($\Delta f = 18 \text{ Hz}$)

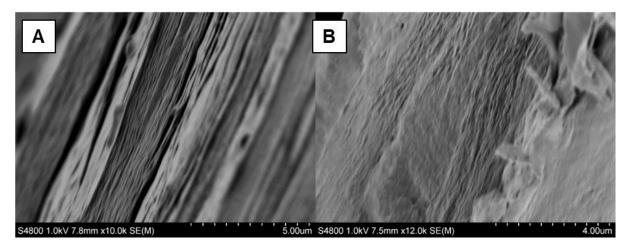


Figure S7. Field emission SEM images recorded for cross-sectioned worm/CNF nanocomposite films comprising 75% CNF by mass, with the remaining 25% mass being made up by either (A) anionic linear PGMA₂₅-PGlyMA₄₅ worms or (B) cationic cross-linked PGMA₂₅-P(Gly-EDA)₄₅ copolymer worms.

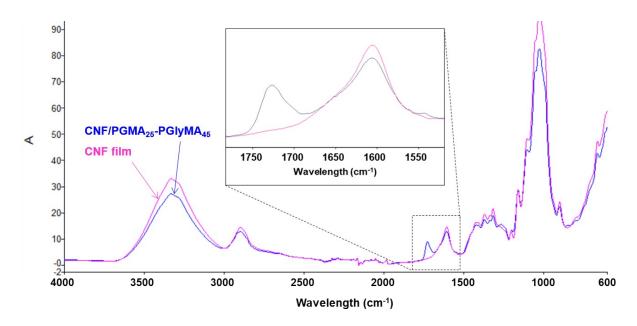


Figure S8. FTIR spectra for the CNF film (pink) and CNF/PGMA₂₅-PGlyMA₄₅ composite film (blue), comprising 25% w/w anionic PGMA₂₅-PGlyMA₄₅ copolymer worms and 75% w/w CNF. Inset shows the region 1500-1790 cm $^{-1}$.