Chemicals and reagents used for polymer synthesis

Poly(ethylene glycol) diol (PEG, hydroxyl value: 110.0 mg KOH.g⁻¹, MW: 1010.81 g.mole⁻¹) was obtained from Acros Organic, while α,ω-bis(6-hydroxyethoxypropyl)-poly(dimethylsiloxane) (PDMS, MW (¹H NMR): 921.49 g.mole⁻¹) was obtained from Shin-Etsu (X-22-160AS). The polyols were dried prior to use at 85-90°C under vacuum (3 x 10⁻³ torr) until the moisture content was less than 0.01 % (as measured by Karl Fisher titration). 1,6-Hexanediisocyanate (HDI, Fluka), anhydrous N,N-dimethylacetamide (DMAc, Sigma Aldrich) and dibutyl tin dilaurate (DBTDL, Merck) were used as received.

Polymer characterisation methods

Proton Nuclear Magnetic Resonance (¹H NMR) spectra were recorded at 400 MHz with a Bruker DPX-400 spectrometer. The NMR spectra refer to solutions in deuterated chloroform (CDCl₃), where the solvent signals were used as internal standards. Resonance peaks were assigned according to the following convention: chemical shift measured in part per million (ppm) relative to the solvent, multiplicity, coupling constants (J Hz), number of protons, and assignments. Multiplicities are denoted as s (singlet), d (doublet), dd (doublet of doublets), t (triplet), dt (doublet of triplets), td (triplet of doublets), q (quartet) or m (multiplet).

Gel permeation chromatography (GPC) was performed on a Shimadzu system equipped with a CMB-20A controller system, an SIL-20A HT autosampler, an LC-20AT tandem pump system, a DGU-20A degasser unit, a CTO-20AC column oven, an RDI-10A refractive index detector, and 4× Waters Styragel columns (HT2, HT3, HT4, and HT5, each 300 mm × 7.8 mm², providing an
effective molar mass range of 100 - 4 × 10⁶). N,N-Dimethylacetamide (DMAc) (containing 4.34 g L⁻¹ lithium bromide (LiBr)) was used as an eluent with a flow rate of 1 mL/min at 80 °C. Number ($M_n$) and weight average ($M_w$) molar masses were evaluated using Shimadzu LC Solution software. The GPC columns were calibrated with low dispersity polystyrene (PSt) standards (Polymer Laboratories) ranging from 575 to 3,242,000 g mol⁻¹, and molar masses are reported as PSt equivalents. A 3rd-order polynomial was used to fit the log $M_p$ vs. time calibration curve, which was almost linear across the range of molar masses.

Fourier transform infrared (FTIR) spectra were collected on a Perkin Elmer Spectrum 2000 FTIR instrument in attenuated total reflectance (ATR) mode using diamond as the background reference. The infrared data were recorded in wavenumbers (cm⁻¹) with the intensity of the absorption ($ν_{max}$) specified as either strong (s), medium (m), weak (w) and prefixed broad (b) where appropriate.

The thermal transitions of the materials were measured by differential scanning calorimetry (DSC) using a Mettler DSC 30. Approximately 8 mg of polymer was encapsulated in a pierced 40 µL aluminium pan. The sample was heated (under nitrogen, 25 mL.min⁻¹) from 25 to 60 °C at a rate of 10 °C.min⁻¹, held at 60 °C for 1 min, cooled to -50 °C (-10 °C.min⁻¹) and held for 1 min to remove the thermal history of the materials. Finally, the samples were heated from -50 to 200 °C at a rate of 10 °C.min⁻¹. The crystallisation temperature ($T_c$) was identified in the cooling cycle, while the glass transition temperature and melting temperatures ($T_g$ and $T_m$, respectively) were measured in the final heating cycle.

**Polymer synthesis and characterisation**

The polymer was synthesised in two batches using the following general procedure. PEG, PDMS and NMe(EtOH)₂ diols were weighed into a 2-neck, 1 L round bottomed flask equipped with a magnetic stirrer. DMAc (around 230 mL) was transferred via cannula to produce a clear solution of the reactants and DBTDL catalyst (0.01 wt%) was added via syringe. The flask was fitted with an air condenser and the solution was heated to 80°C under N₂ flow before dropwise addition of HDI to the stirring polyol solution. After 16 h, a sample of the polymer solution was taken and analysed by GPC to confirm that the molecular weight of the product was near 60,000 g mole⁻¹ (relative to polystyrene standards). The polymer was isolated after evaporation of the solvent in a vacuum oven overnight at 60°C, 100 mbar.
**Batch 1** was produced from the reaction of PDMS diol (34.1380 g, 37.0 mmole), PEG diol (37.4460 g, 37.0 mmole), NMe(EtOH)$_2$ (8.287 g, 74.1 mmole) and HDI (24.9242 g, 148.2 mmole), which produced 105.3340 g polymer with GPC: $M_n$ 59,200, $M_w/M_n$ 2.03.

**Batch 2** was produced from the reaction of PDMS diol (31.5192 g, 34.2 mmole), PEG diol (34.5257 g, 34.2 mmole), NMe(EtOH)$_2$ (8.1459 g, 68.4 mmole) and HDI (23.0670 g, 137.1 mmole), which produced 97.1212 g polymer with GPC: $M_n$ 68,100, $M_w/M_n$ 1.95.

Since the polymeric products obtained from the aforementioned reactions possessed similar molecular weight distributions by GPC, the products were combined in an acetone solution at a 50:50 weight ratio. After evaporation of the solvent, the blended sample yielded the following characterisation data.

**Characterisation data:** $^1$H NMR: (400 MHz, CDCl$_3$) δ 0.04-0.08 (br, 59.2H, f), 0.48 (m, 4H, e), 1.31 (br. m, 16H, j), 1.48 (br. m, 16H, i), 1.64 (m, 4H, d), 2.34 (s, $J = 6.7$ Hz, 6H, n), 2.68 (br m, 8H, m), 3.13 (m, 16H, h), 3.41 (t, $J = 7.2$ Hz, 16H, h), 3.63 (s, 90.7H, k/b), 4.13 (t, $J = 5.5$ Hz, 8H, l), 4.19 (br m, 8H, a/k'), 4.83 and 4.97 (2 x br. s, 8H, g), H$_2$O signal appeared downfield at 1.88 (refer to Figure S2 for proton assignment codes). IR(ATR): 3339 w, 2956 w, 2924 w, 2866 m, 1717 m, 1536 m, 1465 m, 1344 m, 1257 s, 1090 s, 1018 s, 963 m, 839 w, 794 s, 703 w cm$^{-1}$. GPC: $M_n$ 59,200, $M_w/M_n$ 1.98. DSC: two overlapping endotherms, attributed to $T_g$ 18.7°C (0.75 J g$^{-1}$ K$^{-1}$) and $T_m$ 21.6°C (2.79 J g$^{-1}$).

The infrared spectrum (IR) obtained for the synthesised polymer is given in Figure S1. The presence of urethane-linkages in the material was confirmed in the IR spectrum characterised by a C=O stretching band at 1717 cm$^{-1}$, urethane N-H stretching at 3339 cm$^{-1}$ and N-H bending vibrations at 1257 cm$^{-1}$. The amphiphilic material, containing both PDMS and PEG repeat segments could be clearly identified, due to the presence of characteristic bands at 794 and 1090 cm$^{-1}$ (arising from Si-CH$_3$ and CH$_2$-O vibrations, respectively).
Figure S1. IR(ATR) Spectrum obtained for the blended polymer

\(^1\)H NMR spectroscopy was used to further confirm the anticipated polymer structure, with the structural assignment provided in Figure S. \(^1\)H NMR data confirmed the presence of major hydrophobic PDMS (f) and hydrophilic PEG-derived components (k and k'), as well as the desired soil-anchoring segments (l, m, n). Water appeared to hydrogen bond with tertiary amine segments, leading to a down field shift in the water signal (δ 1.88 ppm).

Figure S2. \(^1\)H NMR Spectrum obtained for the blended polymer in CDCl₃
Preparation of small-scale aqueous batch for use in laboratory pot-trials

The polymer (9.27 g) was dissolved in acetone (15.0 g) by stirring for 0.5 h. The polymer solution was added dropwise to stirring 0.3% aqueous sodium dodecyl sulphate (347.3 g). The mixture was left stirring overnight under a stream of compressed air. The following day, no smell of acetone was detected by nose and the total mass of the solution was adjusted with \( \text{H}_2\text{O} \) to give 2.6% (w/w) polymer suspension. The solution appeared turbid with some small gelatinous particles observed when the suspension washed onto the sides of the glass bottle. To produce a lower particle size, higher shear forces were required. The suspension was therefore mixed over a period of 4 h using an overhead stirrer and castellated stirring rod. The resulting suspension was sprayable from an Aqua systems multipurpose sprayer (500 mL) obtained from Bunnings.

Laboratory pot trial to establish baseline polymer performance in minimising soil water evaporation

The baseline performance of the polymer as a barrier to minimise soil water evaporation was examined on a clay and sandy loam. In these experiments, pots (h 20 x d 20 cm) were filled with a ca. 3.1 kg of soil and the aqueous polymer suspension was sprayed onto the surface of the soil at an application loading of ~50 g polymer m\(^{-2}\). The pot was placed in a fume hood and left to dry overnight (ca. 16 h). The pot was placed in a dish containing deionised water and wet to a standard water content (as indicated by glistening of water at the soil surface). The base of the
pot was blotted dry with paper towel and was placed on individual balances in a temperature and humidity controlled room (maintained at 30°C, 40%RH) with the mass being automatically recorded every 15 min for 72 h. The mass loss from the pots over the 72 h period was attributed to soil water evaporation. Three replicates of the treatment and three controls (with no polymer applied) were run simultaneously. The weight data was used to construct plots of time (h) versus cumulative water loss (g) for each sample. The rate of evaporative water loss (g h⁻¹) was determined from the gradient of the initial linear portion of the curve. Multiplication of the rate by 24 h, gave an approximation of the rate of daily soil water evaporation (g day⁻¹) that could be directly compared with those estimated during the glasshouse experiment.

Table S1. Soil water evaporation for non-treated and polymer-treated soils (30°, 40%RH)

| Sub-surface watering | Sandy loam (g day⁻¹) | % Reduction due to polymer | Clay (g day⁻¹) | % Reduction due to polymer |
|----------------------|----------------------|---------------------------|----------------|---------------------------|
| No polymer           | 83.3                 |                           | 69.4           |                           |
| With polymer (50 g m⁻²) | 40.3               | 51.6%                     | 45.6           | 34.2%                     |
| Surface watering     |                      |                           |                |                           |
| No polymer           | 84.5                 |                           | 89.3           |                           |
| With polymer (50 g m⁻²) | 38.2               | 54.8%                     | 70.1           | 21.5%                     |

Preparation of large-scale aqueous polymer formulation for use in the glasshouse experiment

Polymer (120 g) was dissolved in acetone (196 g and added dropwise to 0.3% aqueous sodium dodecyl sulphate (4495 g) and stirred with the aid of an overhead stirrer set to 500 rpm. The suspension was left to stir overnight, open to the atmosphere to evaporate acetone. The following day, the suspension was made up to a total mass of (4615 g) with water. It was divided in to two and mixed again at high speed using a Polytron PT10-39GT homogeniser (Patheck, Australia) (15000 rpm, 20 min) to generate the final sprayable suspension (containing 2.6 wt% polymer). A sample of the suspension (40 mL) was stored in laboratory conditions for particle size analysis, and the remainder was shipped to Narrabri for use in the glasshouse experiment.

Characterisation of aqueous formulation used in glasshouse experiment

The stability of the polymer suspension was monitored using a particle sizing technique (Dynamic Light Scattering (DLS)), over a period of 26 days. Monitoring particle size provides some insight into the potential shelf life of aqueous formulations as an increasing particle sizes typically
indicates reducing formulation stability. The DLS results, measuring cumulant particle size (nm), obtained over the analysis period (days) are presented in Figure S4.

![Figure S4. Changes to cumulant particle size of polymer suspension over 26 days](image)

The average particle size measured 3 days after preparation of the suspension was 76 nm (Figure S4). The particle size distribution was trimodal, comprising 16.6% particles with diameters of 20 nm, 79.5% of particles with diameters of 134 nm, and 3.8% of particles with diameters of 4577 nm. This trimodal distribution indicates that further optimisation of the suspension protocol will be required to achieve a physically stable, well-defined and unimodal particle size distribution.

After 5 days, the cumulant particle size increased approximately three-fold to 226.5 nm with the proportion of larger particles in the sample increasing (from 3.8% to 56.3% > 4 µm). This indicated that the aqueous polymer suspension was physically unstable. As the particle size increases, suspended polymer particles become more susceptible to sedimentation due to gravitational forces and may affect the sprayability of the product possibly causing blockages in the spray nozzles. Nevertheless, the polymer suspension was 5 days old before it was used in the glasshouse experiment and despite the increased cumulant particle size, it remained easy to spray and apply to soil.
Soil chemical data obtained prior to starting the glasshouse experiment

Table S2. Full chemical analysis data of soils prior to N supplementation in glasshouse

| Method    | Nutrient                  | Units   | Sandy loan | Clay  |
|-----------|---------------------------|---------|------------|-------|
| Morgan 1  | Calcium                   | Ca      | 1141       | 1713  |
|           | Magnesium                 | Mg      | 313        | 500   |
|           | Potassium                 | K       | 86         | 163   |
|           | Phosphorus                | P       | 5.3        | 8.7   |
| Bray1     | Phosphorus                | P       | 30         | 59    |
| Colwell   | Phosphorus                | P       | 59         | 105   |
| Bray2     | Nitrate Nitrogen          | N       | 13         | 24    |
| KCl       | Ammonium Nitrogen         | mg/kg   | 1.9        | 1.9   |
|           | Sulfur                    | S       | 9.3        | 7.7   |
| 1:5 Water | pH                        | units   | 7.46       | 7.51  |
|           | Conductivity              | dS/m    | 0.095      | 0.124 |
| Calculation| Estimated Organic Matter | % OM    | 1.3        | 2.1   |
| Ammonium Acetate Calculations | Calcium | Ca | 9.29 | 17.50 |
|           | Magnesium                 | Mg      | 4172       | 7858  |
|           |                           |         | 1863       | 3508  |
|           |                           |         | 3.92       | 7.36  |
|           | Potassium                 | K       | 1067       | 2002  |
|           | Sodium                    | Na      | 477        | 894   |
|           |                           |         | 0.51       | 1.65  |
|           |                           |         | 0.29       | 0.24  |
|           |                           |         | 152        | 122   |
|           |                           |         | 68         | 54    |
|           | KCl                       | Al      | 12         | 2     |
|           |                           |         | 6          | 1     |
|           | Acidity Titration         | Hydrogen| H⁺         | 0.00  | 0.00  |
| Calculation| Effective Cation Exchange Capacity (ECEC) | cmol⁺/kg | 14.08 | 26.76 |
| Base Saturation Calculations | Calcium | Ca | % | Magnesium | Mg | % | Potassium | K | % | Sodium - ESP | Na | % | Aluminium | Al | % | Hydrogen | H+ | % |
|-------------------------------|---------|----|---|-----------|----|---|----------|---|---|-------------|----|---|-----------|----|---|----------|----|---|
|                               |         | 66.0 | 65.4 | 27.8 | 27.5 | 3.6 | 6.2 | 2.1 | 0.9 | 0.4 | 0.0 | 0.0 | 0.0 |
| Calculation                  | Calcium / Magnesium Ratio | ratio | 2.4 | 2.4 |
| DTPA                         | Zinc    | Zn | mg/kg | 0.6 | 0.9 |
|                              | Manganese | Mn | mg/kg | 11 | 11 |
|                              | Iron    | Fe | mg/kg | 61 | 42 |
|                              | Copper  | Cu | mg/kg | 1.2 | 1.8 |
| CaCl₂                        | Boron   | B  | mg/kg | 0.36 | 0.63 |
|                              | Silicon | Si | mg/kg | 44 | 64 |
| LECO IR Analyser             | Total Carbon | C | % | 0.74 | 1.19 |
|                              | Total Nitrogen | N | % | 0.07 | 0.11 |
| Calculation                  | Carbon/ Nitrogen Ratio | ratio | 11.4 | 10.5 |
| Basic Texture                | Loam    | Loam |
| Basic Colour                 | Brownish | Brownish |
| Calculation                  | Chloride Estimate | equiv. ppm | 61 | 79 |
Glasshouse trial pot layout

Figure S5. Pot layout showing treatments and bench positions
Additional schemes and figures referred to in manuscript text

Scheme S1. The influence of pH on soil anchoring groups in the polymer

Figure S6. Photograph showing spray application of the polymer formulation on to pots in the glasshouse. Credit: Dr Michael Braunack (CSIRO Agriculture and Food).

Figure S7. Photographs of sandy loam subjected to surface watering regime with and without polymer treatment.

Figure S8. Soil pH measured at harvest.