Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Aqueous one-pot synthesis of epoxy-functional diblock copolymer worms from a single monomer: new anisotropic scaffolds for potential charge storage applications

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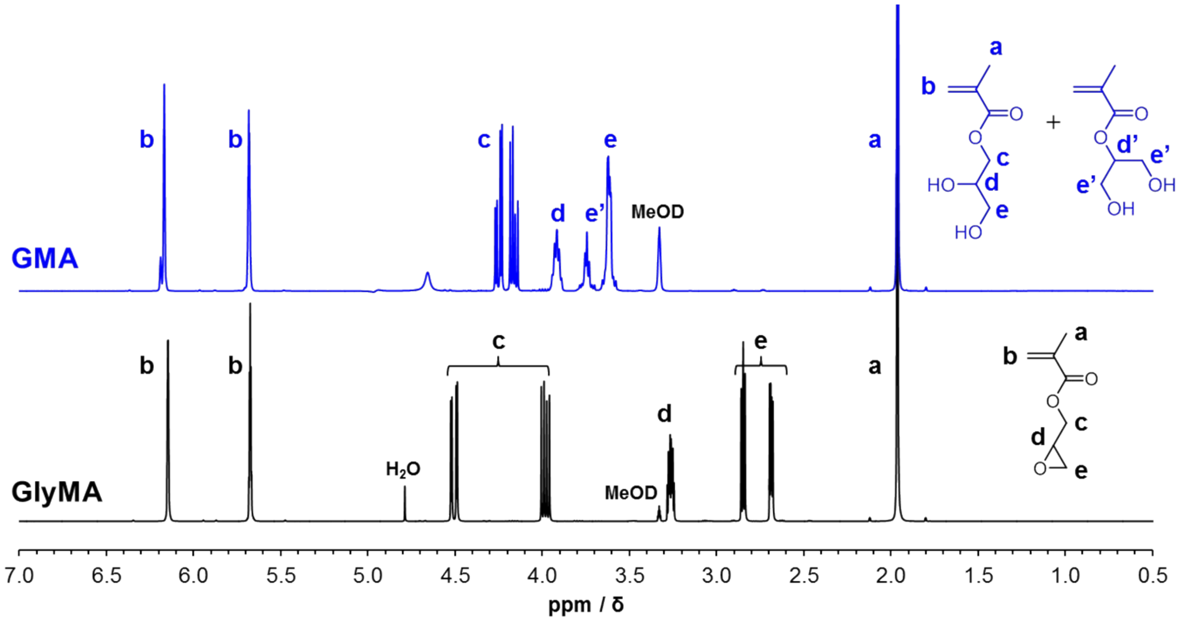

Figure S1. ^{1}H NMR (400 MHz, CD_3OD) spectra obtained for glycidyl methacrylate (GlyMA) and after its hydrolysis to afford glycerol monomethacrylate (GMA). The GMA spectrum was recorded using solvent suppression of the water peak.

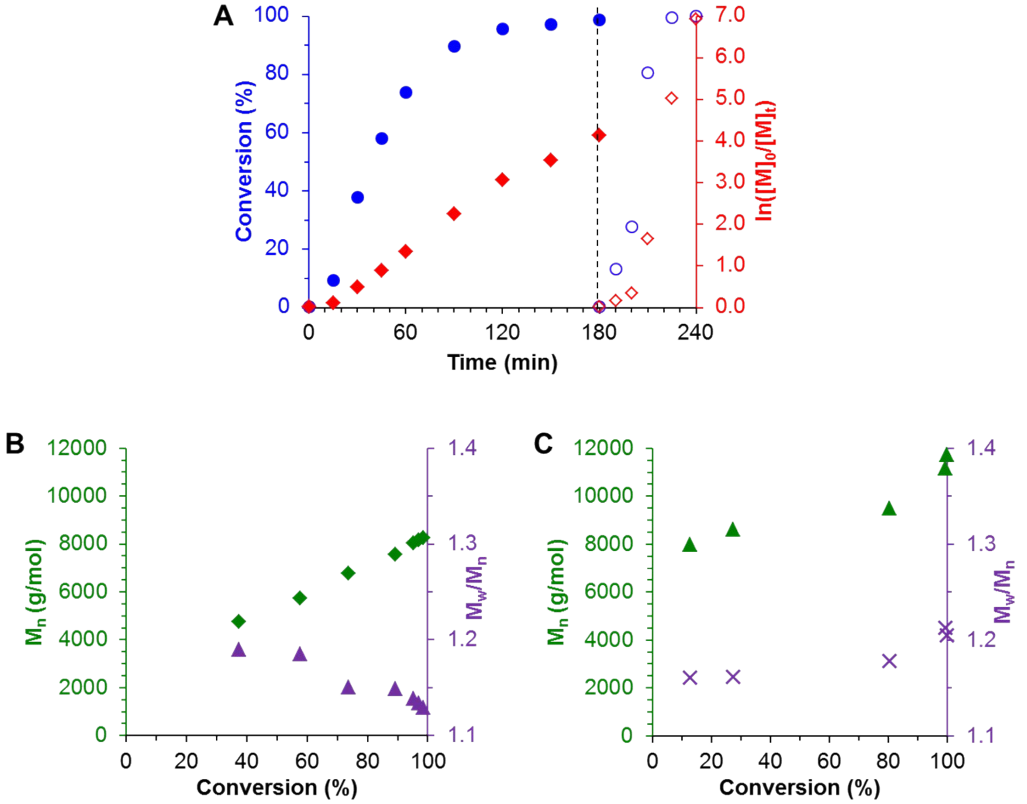

Figure S2. Kinetics of the RAFT aqueous solution polymerization of GMA and subsequent chain extension of the resulting water-soluble PGMA precursor via RAFT aqueous emulsion polymerization of GlyMA, targeting a $PGMA_{25}$-$PGlyMA_{45}$ diblock composition. (A) Conversion *vs.* time curves obtained from ^{1}H NMR studies, and the evolution of M_n and M_w/M_n with conversion for (B) the RAFT aqueous solution polymerization of GMA and (C) the RAFT aqueous emulsion polymerization of GlyMA.

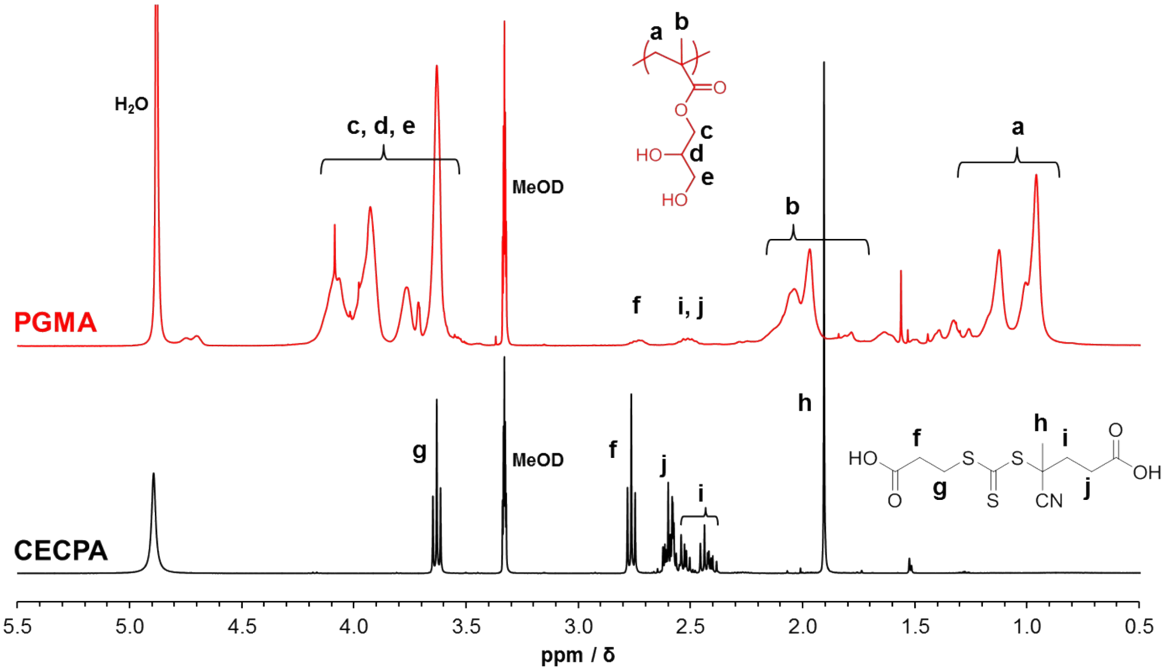

Figure S3. ^{1}H NMR (400 MHz, CD_3OD) spectra recorded for 4-((((2-carboxyethyl)thio)carbonothioyl)thio)-4-cyanopentanoic acid (CECPA) and poly(glycerol monomethacrylate) ($PGMA_{25}$) after purification by precipitation. End-group analysis of the PGMA precursor indicated a mean DP of 25, when targeting a mean DP of 20, suggesting a CECPA RAFT agent efficiency of 80%. The DP was calculated by end-group analysis by comparing the integrated intensity for signal *f* (2.73 ppm), which is assigned to two HOOC-C$\underline{H}_2$ protons located on chain-ends derived from the CECPA RAFT agent, to that of signals *c*, *d* and *e* assigned to the five protons on the pendent glyceryl groups (3.5-4.2 ppm) of the GMA repeat units.

Table S1. Summary of conversion and molecular weight data obtained for five RAFT solution polymerizations of GMA (obtained via hydrolysis of GlyMA) at 11.2% w/w, when targeting a mean DP of 25 using CECPA as the chain transfer agent. The CTA/VA-044 molar ratio was 4.0 in all cases and each polymerization was conducted at 50 °C for 3 h at a solution pH of 2.5-3.0. These five entries suggest good reproducibility for the synthesis of the $PGMA_{25}$ precursor via RAFT aqueous solution polymerization of GMA.

Entry no.	Target Composition	Conversion (%) [a]	M_n (g mol^{-1}) [b]	M_w (g mol^{-1}) [b]	M_w/M_n [b]
1	$PGMA_{25}$	>99	7,900	9,050	1.14
2	$PGMA_{25}$	98.4	8,200	9,300	1.13
3	$PGMA_{25}$	>99	8,200	9,000	1.11
4	$PGMA_{25}$	>99	8,050	8,900	1.11
5	$PGMA_{25}$	>99	8,300	9,300	1.12

[a] Determined by ^{1}H NMR spectroscopy using d_6-DMSO. [b] Determined by gel permeation chromatography analysis using DMF eluent containing 10 mM LiBr, a refractive index detector and calibration against a series of near-monodisperse poly(methyl methacrylate) standards.

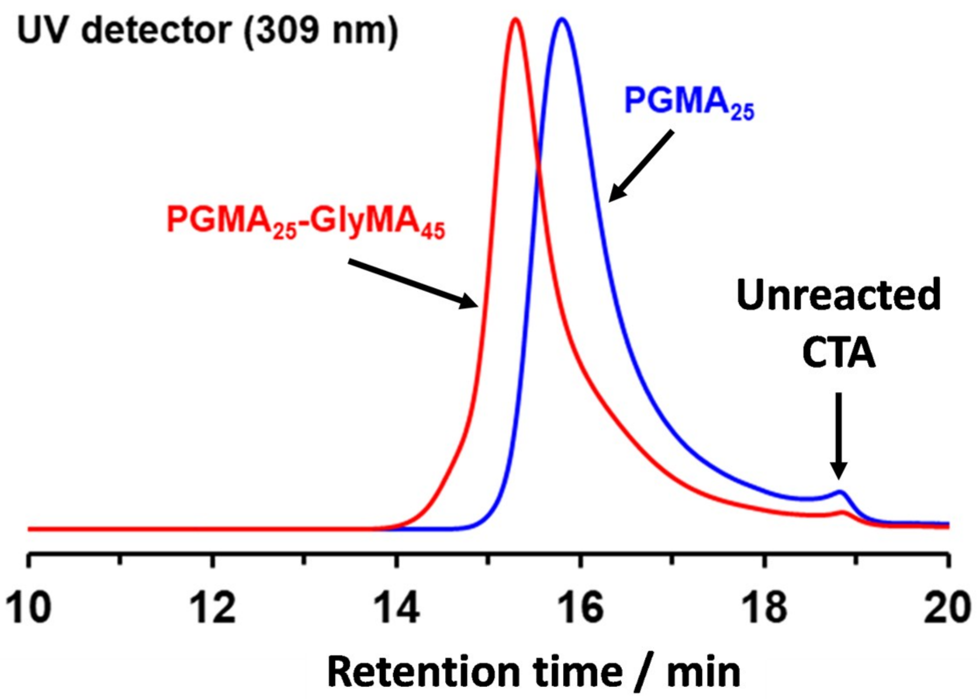

Figure S4. Normalized UV GPC chromatograms for a $PGMA_{25}$ macro-CTA and the corresponding $PGMA_{25}$-$PGlyMA_{45}$ diblock copolymer after chain extension. The small peak at 18.8 min corresponds to unreacted CTA. ($PGMA_{25}$ M_n = 8 000 g mol^{-1}, $Đ$ = 1.22; $PGMA_{25}$-$PGlyMA_{45}$: M_n = 12 600 g mol^{-1}, $Đ$ = 1.32).

Table S2. Summary of conversion, molecular weight and DLS data for various $PGMA_{25}$-$PGlyMA_x$ diblock copolymer worms prepared by chain extension of a $PGMA_{25}$ macro-CTA via RAFT aqueous emulsion polymerization of GlyMA at 15% w/w. All syntheses were conducted at 50 °C for 2 h at a solution pH of 2.5-3.0.

Target Composition	Conversion (%) [a]	M_n (g mol^{-1}) [b]	M_w (g mol^{-1}) [b]	M_w/M_n [b]	D_{DLS} (nm)	PDI
$PGMA_{25}$-$PGlyMA_{25}$	>99	10 400	12 600	1.21	19	0.14
$PGMA_{25}$-$PGlyMA_{40}$	>99	12 100	14 700	1.21	143	0.48
$PGMA_{25}$-$PGlyMA_{45}$	>99	12 500	15 500	1.23	324	0.50
$PGMA_{25}$-$PGlyMA_{50}$	>99	12 500	15 800	1.27	306	0.66
$PGMA_{25}$-$PGlyMA_{55}$	>99	13 000	16 600	1.27	384	0.56
$PGMA_{25}$-$PGlyMA_{60}$	>99	13 900	17 500	1.26	262	0.26

[a] Determined by ^1H NMR spectroscopy using d_6-DMSO. [b] Determined by gel permeation chromatography analysis using DMF eluent containing 10 mM LiBr, a refractive index detector and calibration against a series of near-monodisperse poly(methyl methacrylate) standards.

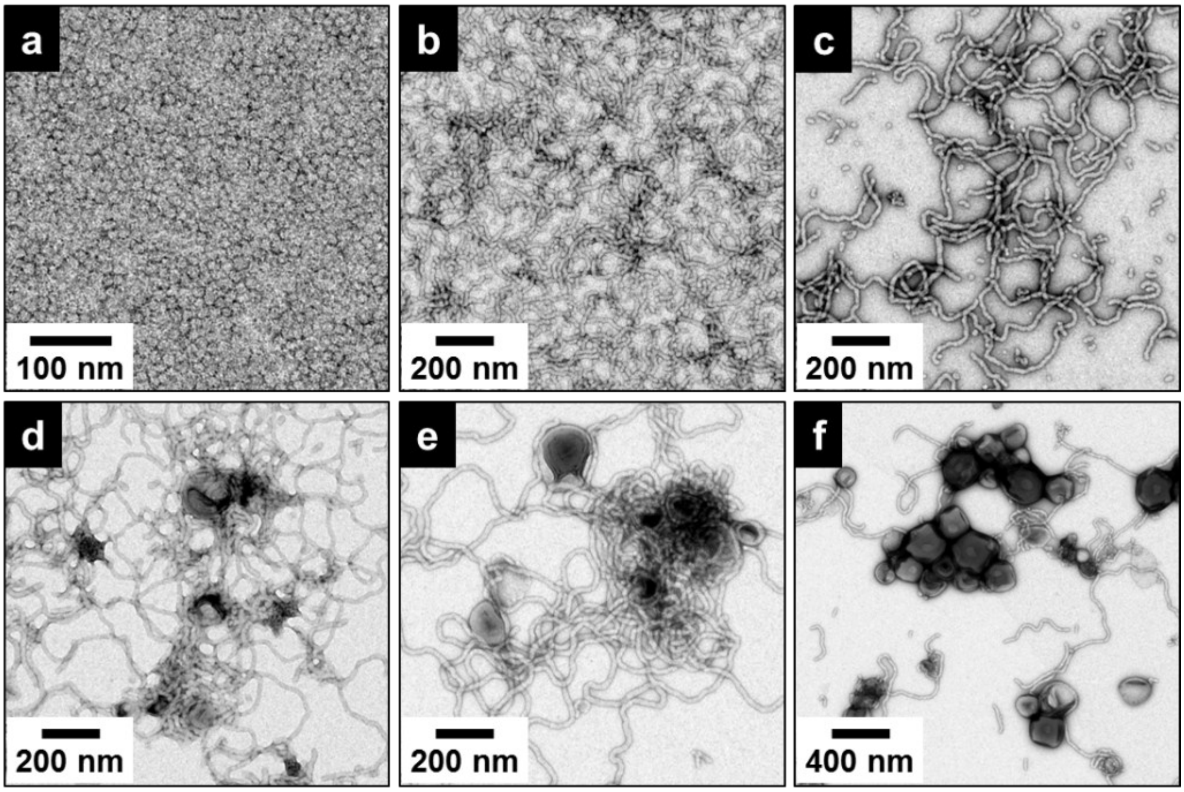

Figure S5. Representative TEM images obtained for PGMA$_{25}$-PGlyMA$_x$ diblock copolymer nanoparticles prepared at 15% w/w by RAFT aqueous emulsion polymerization of GlyMA [x = 25 (a), 40 (b), 45 (c), 50 (d), 55 (e) and 60 (f)].

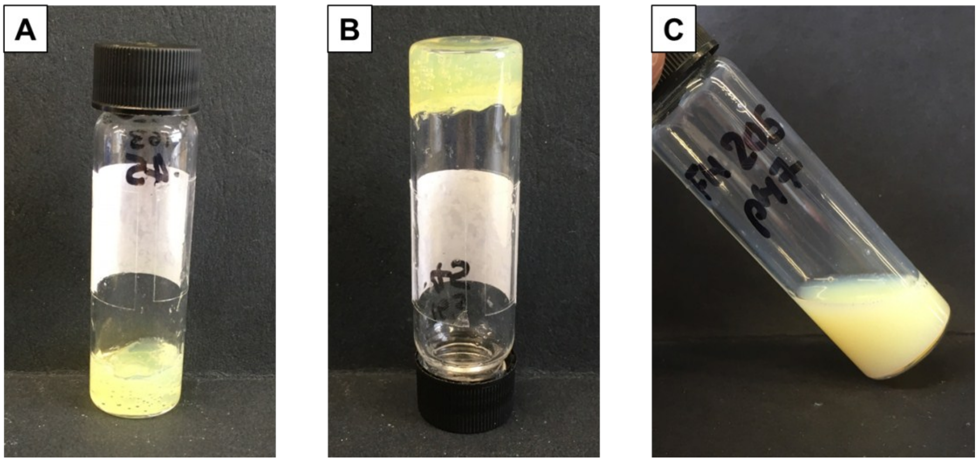

Figure S6. Digital photographs recorded for an as-synthesized PGMA$_{25}$-PGlyMA$_{45}$ worm gel prepared at 15% w/w via RAFT aqueous emulsion polymerization of GlyMA using a PGMA$_{25}$ precursor at pH 3 (A). Tube inversion (B) confirms the free-standing nature of this physical aqueous gel. The same polymerization conducted at pH 7 (C) gave a turbid free-flowing liquid indicating that the formation of worms was inhibited, limiting the morphology to spheres, due to ionization of the carboxylic acid groups present at the chain ends from the CTA.

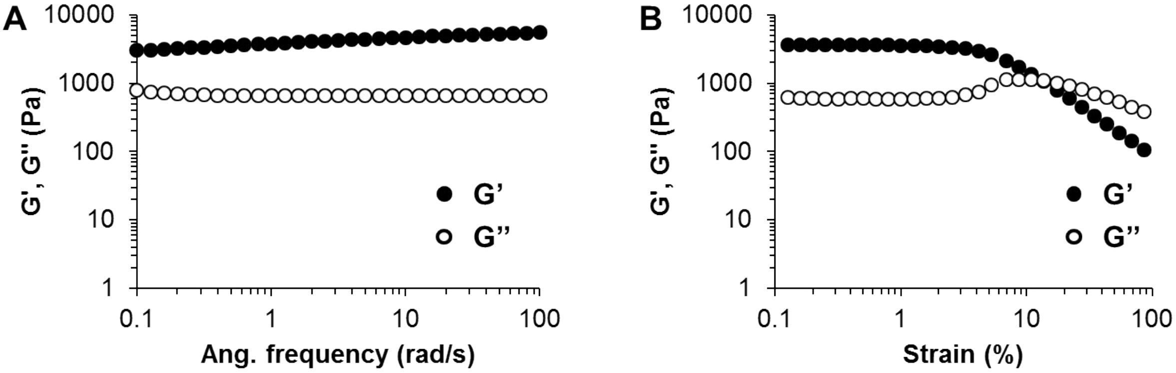

Figure S7. Rheological frequency sweep (A) and strain sweep (B) showing G' (closed symbols) and G'' (open symbols) for the PGMA$_{25}$-PGlyMA$_{45}$ diblock copolymer worm gel at 15% w/w.

Table S3. Nitrogen contents (%) and corresponding mean degrees of derivatization calculated for the 4-amino-TEMPO derivatized PGMA$_{25}$-PGlyMA$_{45}$ diblock copolymer worms using elemental microanalysis. Epoxy-amine reactions were conducted using copolymer concentrations of 2.5-7.5% w/w at 50-70 °C for 3 to 24 h.

Diblock copolymer concentration (% w/w)	Temperature (°C)	Time (h)	4-aminoTEMPO /epoxy molar ratio	N% content	Degree of derivatization (%)[a]
2.5	50	6	1.50	4.48	64.7
		24	1.50	4.69	67.8
	70	6	1.50	4.87	70.4
		24	1.50	4.93	71.2
		24	2.00	5.12	74.0
		24	4.00	5.53	79.9
5.0	50	6	1.00	4.81	69.5
		6	1.25	4.87	70.4
		6	1.50	5.27	76.2
		6	2.00	5.94	85.8
		6	4.00	6.04	87.3
		24	1.50	5.26	76.0
	60	6	1.50	5.62	81.2
		6	2.00	5.32	76.9
		6	4.00	*	*
	70	6	1.50	5.17	74.7
		24	1.50	5.06	73.1
6.0	50	6	1.50	*	*
	60	6	1.50	*	*
	70	6	1.50	*	*
7.5	50	6	1.50	*	*
	70	6	1.50	*	*

[a] Calculated using: Degree of derivatization = (experimental N% content / theoretical N% content) x 100, where the theoretical maximum N% content is 6.92% (assuming quantitative reaction).

* Sample formed an insoluble, non-redispersible chemical gel

Table S4. DLS z-average diameters, D_z, polydispersity indices and derived count rates recorded for the precursor PGMA$_{25}$-PGlyMA$_{45}$ diblock copolymer worms and 4-aminoTEMPO derivatized worms at copolymer concentrations of 0.1% w/w in either deionised water or DMF.

Diblock copolymer	DLS in H_2O			DLS in DMF		
	D_z (nm)	PDI	Derived Count Rate (kcps)	D_z (nm)	PDI	Derived Count Rate (kcps)
PGMA$_{25}$-PGlyMA$_{45}$	144	0.30	16982	1601	0.93	125
PGMA$_{25}$-P(GlyMA-NH-TEMPO)$_{45}$	194	0.42	14595	203	0.45	4234

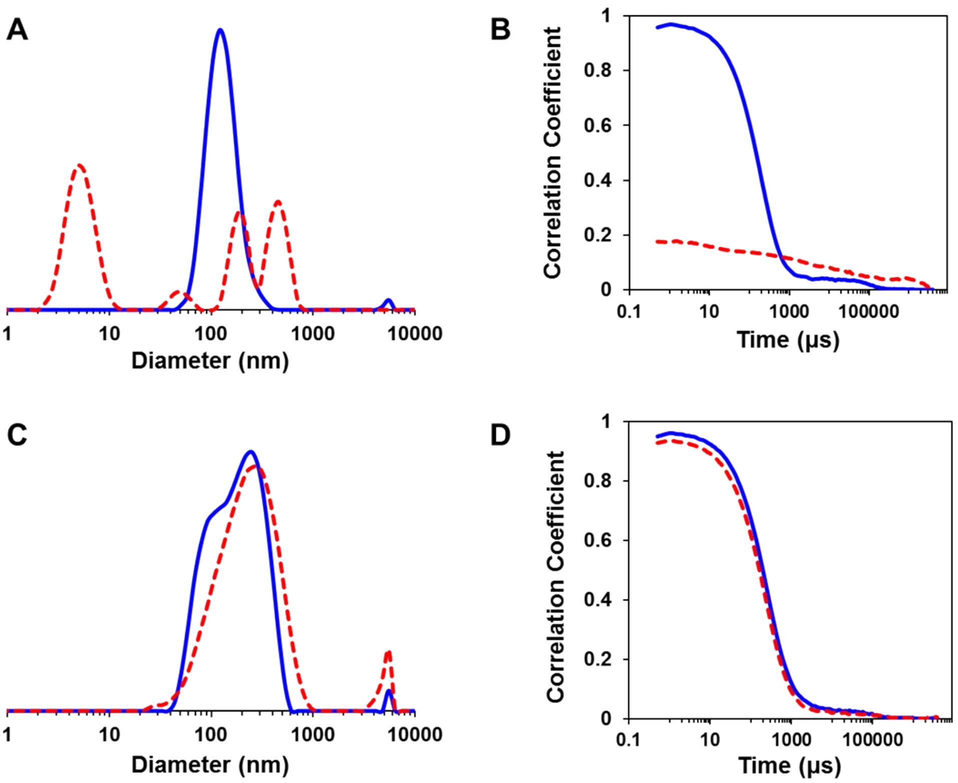

Figure S8. DLS size distributions by intensity (A) and corresponding correlograms (B) for the precursor PGMA$_{25}$-PGlyMA$_{45}$ diblock copolymer worms, and the DLS size distributions by intensity (C) and corresponding correlograms (D) for the 4-aminoTEMPO derivatized worms. In each case the copolymer was diluted to 0.1% w/w in either water (blue solid lines) or DMF (red dashed lines). As the precursor PGMA$_{25}$-PGlyMA$_{45}$ diblock copolymer chains are fully dissolved in DMF they do not scatter enough to obtain a satisfactory correlation function (B). Therefore, poor fitting of the correlation function is inaccurately represented as multiple populations in the size distribution by intensity plot.

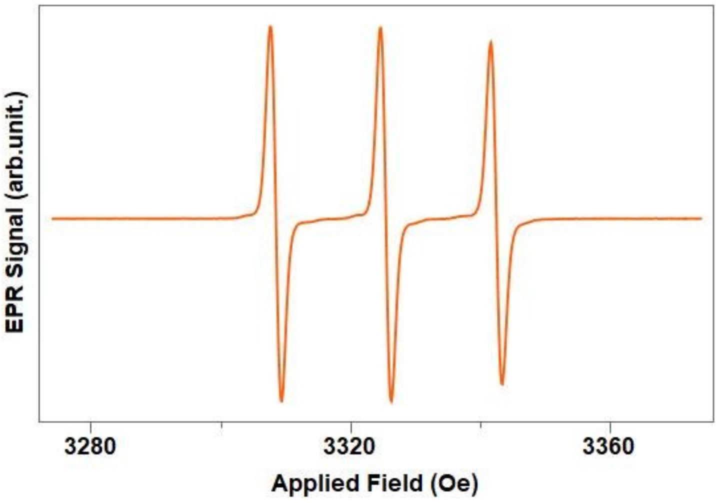

Figure S9. EPR spectrum recorded for a 1 mM aqueous solution of the 4-amino-TEMPO small molecule precursor, showing only sharp triplet signals for the unpaired electrons of this stable nitroxide species.

SAXS Model

In general, the intensity of X-rays scattered by a dispersion of nano-objects [usually represented by the scattering cross-section per unit sample volume, $\frac{d\Sigma}{d\Omega}(q)$] can be expressed as:

$$\frac{d\Sigma}{d\Omega}(q) = NS(q)\int_0^\infty \dots \int_0^\infty F(q,r_1,\dots,r_k)^2\Psi(r_1,\dots,r_k)dr_1,\dots,dr_k$$

Equation S1

where $F(q,r_1,\dots,r_k)$ is the form factor, $r_1,\dots,r_k$ is a set of *k* parameters describing the structural morphology, $\Psi(r_1,\dots,r_k)$ is the distribution function, *S*(*q*) is the structure factor and *N* is the number density per unit volume of nano-object expressed as:

$$N = \frac{\varphi}{\int_0^\infty \dots \int_0^\infty V(r_1,\dots,r_k)\Psi(r_1,\dots,r_k)dr_1,\dots,dr_k}$$

Equation S2

where $V(r_1,\dots,r_k)$ is the volume of the nano-object and φ is the nano-object volume faction.

Worm-like micelle model

The worm-like micelle form factor for Equation S1 is given by:

$$F_{w\_mic}(q) = {N_w}^2{\beta_s}^2F_{sw}(q) + N_w{\beta_c}^2F_c(q,R_g) + N_w(N_w - 1){\beta_c}^2S_{cc}(q) + 2{N_w}^2\beta_s\beta_cS_{sc}(q)$$

Equation S3

where the core block and corona block X-ray scattering length contrast are given by $\beta_s = V_s(\xi_s - \xi_{sol})$ and $\beta_c = V_c(\xi_c - \xi_{sol})$ respectively. Here ξ_s, ξ_c and ξ_{sol} are the X-ray scattering length densities of the core block (ξ_{PGlyMA}= 11.34 x 10^{10} cm^{-2}), corona block (ξ_{PGMA}= 11.94 x 10^{10} cm^{-2}) and solvent (ξ_{sol}= 9.42 x 10^{10} cm^{-2}), respectively. V_s is the volume of the core block (V_{PGlyMA}) and V_c is the volume of the corona block (V_{PGMA}). These volumes were calculated using $= \frac{M_{n,pol}}{N_A\rho}$, where the solid-state density of PGlyMA homopolymer, ρ_{PGlyMA}, was determined by helium pycnometry to be 1.25 g cm^{-3} and the density of PGMA, ρ_{PGMA}, was taken to be 1.31 g cm^{-3}.[3] $M_{n,pol}$ corresponds to the number-average molecular weight of the an individual diblock copolymer chain as determined by ^1H NMR spectroscopy.

The self-correlation term for the worm-like micelle core of radius R_{sw} is:

$$F_{sw}(q) = F_{worm}(q,L_w,b_w){A_{CSworm}}^2(q,R_{sw})$$

Equation S4

which is a product of a core cross-section term:

$$F_{CSworm}(q,R_g) = A_{CSworm}{}^2(q,R_{sw}) = \left[2\frac{J_1(qR_{sw})}{qR_{sw}}\right]^2$$

Equation S5

where J_1 is the first-order Bessel function of the first kind, and a form factor $F_{worm}(q,L_w,b_w)$ for self-avoiding semi-flexible chains represents the worm-like micelles, where b_w is the Kuhn length and L_w is the mean contour length. A complete expression for the chain form factor can be found elsewhere.[4] The self-correlation term for the corona block is given by the Debye function:

$$F_c(q,R_g) = \frac{2\left[\exp\left(-q^2R_g{}^2\right) - 1 + q^2R_g{}^2\right]}{q^4R_g{}^4}$$

Equation S6

where R_g is the radius of gyration of the PGMA coronal block. The aggregation number of the worm-like micelle is:

$$N_w = (1 - x_{sol})\frac{\pi R_{sw}{}^2L_w}{V_s}$$

Equation S7

where x_{sol} is the volume fraction of solvent within the worm-like micelle core. Possible semi-spherical caps at the ends of each worm are not considered in this form factor.

References

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