Supporting information: Microstructural dynamics and rheology of worm-like diblock copolymer nanoparticle dispersions under a simple shear and a planar extensional flow

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1 Synthesis and characterization

1.1 Materials

Stearyl methacrylate (SMA) was purchased from Santa Cruz Biotechnology, Inc. (USA) and was used as received. Methyl methacrylate (MMA, 99%) was purchased from Alfa Aesar (Germany), passed through basic alumina to remove its inhibitor and then stored at –20 °C prior to use. Benzyl methacrylate (BzMA, 96%), 2-cyano-2-propyl dithiobenzoate (CPDB), CDCl₃ and n-dodecane were purchased from Merck (UK) and used as received. 2,2’-Azobisobutyronitrile (AIBN) was obtained from Molekula (UK) and tert-butyl peroxo-2-ethylhexanoate (T21s) was purchased from AkzoNobel (The Netherlands). CD₂Cl₂ was purchased from Goss Scientific (UK). Tetrahydrofuran was obtained from VWR Chemicals (UK). Ethanol and toluene were purchased from Fisher Scientific (UK). API Group III mineral oil (shear viscosity = 3.1 mPa s at 100 °C and 24.5 mPa s at 22 °C) was kindly provided by The Lubrizol Corporation Ltd. (Hazelwood, Derbyshire, UK).

1.2 Synthesis of PSMA₁₀ precursor via RAFT solution polymerization in toluene

The PSMA₁₀ precursor was synthesized at 50% w/w solids as follows. SMA (66.0 g; 195.0 mmol), CPDB (4.8 g; 21.7 mmol; target degree of polymerization, DP = 9), AIBN (712 mg; 4.3 mmol; CPDB/AIBN molar ratio = 5.0) and toluene (71.5 g) were weighed into a 250 mL round-bottomed flask. The sealed flask was purged with nitrogen for 30 min and immersed in a preheated oil bath at 70 °C. The ensuing polymerization was quenched after 4 h by exposing the reaction solution to air and cooling the flask to room temperature. A final SMA conversion of 70% was determined by ¹H NMR (nuclear magnetic resonance) spectroscopy. The crude polymer was purified by three consecutive precipitations into a ten-fold excess of ethanol (with redissolution in THF after precipitation). The mean DP of the precursor block was calculated to be 10 by using ¹H NMR spectroscopy to compare the aromatic protons assigned to the dithiobenzoate end-group at 7.3-8.0 ppm to the two oxymethylene protons attributed to PSMA at 3.8-4.2 ppm. Tetrahydrofuran (THF) gel permeation chromatography (GPC) analysis using a refractive index detector and a series of near-monodisperse poly(methyl methacrylate) standards indicated an $M_n$ of 4.4 kg mol⁻¹ and $M_w/M_n = 1.13$ (Fig. S1).

1.3 Synthesis of poly(stearyl methacrylate)-poly(methyl methacrylate) (PSMA₁₀-PMMA₈₃) S-WLNP via RAFT dispersion polymerization of MMA in mineral oil

The synthesis of PSMA₁₀-PMMA₈₃ nanoparticles (S-WLNP) at 20% w/w solids was conducted as follows. PSMA₁₀ precursor (5.00 g; 1.39 mmol), T21s initiator (99.94 mg; 462.06 µmol; 10.0% v/v in mineral oil) and mineral oil (67.13 g) were weighed into a 250 mL round-bottomed flask and purged with nitrogen for 30 min. MMA monomer (12.40 mL; 116.44 mmol; target DP = 84) was degassed separately then added to the reaction mixture via a syringe. The sealed round-bottomed flask was immersed in a preheated oil bath at 90 °C and the reaction mixture was magnetically stirred for 17 h. ¹H NMR analysis indicated
an MMA conversion of 99% was determined by comparing the integrated methyl signal assigned to MMA monomer at 3.75–3.78 ppm to that of the copolymer at 3.50–3.72 ppm at the end of the copolymerization. THF GPC analysis indicated an $M_n$ of 13.2 kg mol$^{-1}$ and an $M_w/M_n$ of 1.10 (Fig. S1). Dynamic light scattering (DLS) analysis of the nanoparticles indicated a z-average diameter of 124 nm ($d_{DLS}$) with a polydispersity index (PDI) of 0.26.

1.4 Synthesis of poly(stearyl methacrylate)-poly(benzyl methacrylate) (PSMA$_{10}$-PBzMA$_{49}$) L-WLNP via RAFT dispersion polymerization of BzMA in mineral oil

The synthesis of PSMA$_{10}$-PBzMA$_{49}$ nanoparticles (L-WLNP) at 10% w/w solids was conducted as follows. PSMA$_{10}$ precursor (2.20 g; 609.92 µmol), BzMA (5.37 g; 30.50 mmol; target DP = 50), T21s initiator (26.39 mg; 121.98 µmol; 10.0% v/v in mineral oil) and mineral oil (68.43 g) were weighed into a 250 mL round-bottomed flask and purged with nitrogen for 30 min. The sealed round-bottomed flask was immersed in a preheated oil bath at 90 °C and the reaction mixture was magnetically stirred for 5 h. $^1$H NMR analysis indicated a BzMA conversion of 97% determined by comparing the integrated oxymethylene signal assigned to BzMA monomer at 5.24–5.28 ppm to that of the copolymer at 4.80–5.20 ppm at the end of the copolymerization. THF GPC analysis indicated an $M_n$ of 11.0 kg mol$^{-1}$ and an $M_w/M_n$ of 1.09 (Fig. S1). DLS analysis of the nanoparticles indicated a z-average diameter of 208 nm ($d_{DLS}$) with a PDI of 0.47.

Figure S 1: GPC curves (vs. a series of near-monodisperse poly(methyl methacrylate) calibration standards) recorded using a refractive index detector for the PSMA$_{10}$ precursor, the PSMA$_{10}$-PMMA$_{83}$ and the PSMA$_{10}$-PBzMA$_{49}$ diblock copolymers.
1.5 ¹H NMR Spectroscopy

¹H NMR spectra were recorded in either CD₂Cl₂ or CDCl₃ using a 400 MHz Bruker Avance spectrometer. Typically, 64 scans were averaged per spectrum.

1.6 Gel Permeation Chromatography (GPC)

Molecular weight distributions (MWDs) were assessed by GPC using THF as an eluent. The GPC system was equipped with two 5 µm (30 cm) mixed C columns and a WellChrom K–2301 refractive index detector operating at 950 ± 30 nm. The THF mobile phase contained 2.0% v/v triethylamine and 0.05% w/v butyl-hydroxytoluene (BHT) and the flow rate was fixed at 1.0 mL min⁻¹. A series of twelve near-monodisperse poly(methyl methacrylate) standards (Mp values ranging from 0.8 to 2200 kg mol⁻¹) were used for column calibration in combination with a refractive index detector.

1.7 Dynamic Light Scattering (DLS)

DLS studies were performed using a Zetasizer Nano ZS instrument (Malvern Instruments, UK) at a fixed scattering angle of 173 °. Copolymer dispersions were diluted in n-dodecane (0.10% w/w) prior to light scattering studies at 20 °C. The intensity-average diameter and polydispersity of the nanoparticles were calculated by cumulants analysis of the experimental correlation function using Dispersion Technology Software version 6.20. Data were averaged over ten runs each of thirty seconds duration. It is emphasized that DLS assumes a spherical morphology. Thus, the DLS diameter calculated for anisotropic nanoparticles such as worms is a “sphere-equivalent” value that indicates neither the worm length nor the worm width. Nevertheless, the “sphere-equivalent” diameter provided by DLS (d_{DLS}) enables to provide a comparative value of the particle size. We note that the root-mean-squared end-to-end length \( \langle R² \rangle^{1/2} \) of the WLNP calculated using eqn. 9 in the main manuscript provides comparable values to the \( d_{DLS} \) (Table S1).

**Table S 1:** Root-mean-squared end-to-end length \( \langle R² \rangle^{1/2} \) of the L-WLNP and S-WLNP calculated using eqn. 9 from the main manuscript with \( \langle l_c \rangle \) and \( l_p = 50 \) nm, and the z-average diameter obtained by DLS \( d_{DLS} \).

|       | \( \langle R² \rangle^{1/2} \) | \( d_{DLS} \) |
|-------|-----------------|-----------|
| L-WLNP (nm) | 254             | 208       |
| S-WLNP (nm)  | 143             | 124       |
2 Shear rheology

The parameters obtained from the Cross model fitting to the flow curves in Fig. 4(a,b) of the main manuscript are given in Table S2 and S3, respectively.

Table S2: Parameters obtained by the Cross model (eqn. 2, main text) for the flow curves of L-WLNP dispersions at different volume fractions ($\phi$) for $\phi \geq 23 \times 10^{-3}$. Fitted curves are shown in the main manuscript.

* Values of $\eta_0$ taken from the viscosity at the lowest accessible shear rate.

** Values of $\eta_\infty$ obtained from eqn. 3 of the main manuscript and used as a fixed parameter for the Cross model.

| $10^3 \phi$ | 4 | 7 | 14 | 23 | 30 | 43 | 49 | 57 | 66 | 72 |
|-------------|---|---|----|----|----|----|----|----|----|----|
| $n$         |   |   |    |    |    |    |    |    |    |    |
| $\eta_0$ (Pa s) | 0.03* | 0.04* | 0.06* | 0.09 | 0.14 | 0.20 | 0.24 | 0.38 | 0.67 | 0.79 |
| $\eta_\infty$ (Pa s)** | 0.028 | 0.030 | 0.035 | 0.042 | 0.048 | 0.058 | 0.062 | 0.068 | 0.075 | 0.080 |
| $\dot{\gamma}$ (1/s) | 21.80 | 21.31 | 22.01 | 24.69 | 16.45 | 8.93 | 7.65 |

Table S3: Parameters obtained by the Cross model (eqn. 2, main manuscript) for the flow curves of S-WLNP dispersions at different volume fractions ($\phi$) for $\phi \geq 57 \times 10^{-3}$. Fitted curves are shown in the main manuscript.

* Values of $\eta_0$ taken from the viscosity at the lowest accessible shear rate.

** Values of $\eta_\infty$ obtained from eqn. 3 of the main manuscript and used as a fixed parameter for the Cross model.

| $10^3 \phi$ | 7 | 17 | 29 | 42 | 57 | 72 | 87 | 102 | 118 | 133 |
|-------------|---|----|----|----|----|----|----|-----|-----|-----|
| $n$         |   |    |    |    |    |    |    |     |     |     |
| $\eta_0$ (Pa s) | 0.03* | 0.04* | 0.07* | 0.12* | 0.33 | 0.67 | 1.22 | 2.48 | 5.65 | 13.89 |
| $\eta_\infty$ (Pa s)** | 0.025 | 0.027 | 0.028 | 0.030 | 0.032 | 0.034 | 0.036 | 0.038 | 0.040 | 0.042 |
| $\dot{\gamma}$ (1/s) | 13.13 | 8.23 | 8.63 | 4.64 | 1.84 | 0.98 |
Figure S 2: Plot of $\tan \delta = G''/G'$ as a function of the scaled angular frequency ($\omega \eta_0/\eta_s$) for the S-WLNP and L-WLNP dispersions above the overlap concentration ($\phi > \phi^*$).

Figure S 3: Relaxation time ($\tau = \dot{\gamma}^{-1}$) obtained from using the Cross model (see eqn. 3 of the main manuscript) to fit the flow curves shown in Fig. 4 of the main manuscript for the S-WLNP and L-WLNP dispersions above the overlap concentration ($\phi > \phi^*$). The solid line indicates a slope of unity as a reference.

3 Birefringence scaling

For each WLNP, the scaling factor ($SF$) for $\dot{\varepsilon}$ required to achieve superposition of the normalized birefringence ($\langle \Delta n \rangle/\phi$) acquired under extensional flow (in the OSCER device) with the $\langle \Delta n \rangle/\phi$ acquired under shear flow (in the SFC device) was obtained using the minimization of the residual squares between the two data sets. Fig. S4(a) presents, as an example, the data sets for the L-WLNP as given in the main text. At first, the two curves were linearly interpolated to construct two data sets with the same $x$-axis (see solid lines in Fig. S4(a)). The interpolation procedure enables to compute the square of the residuals as

$$\text{Residuals}^2(\dot{\gamma}) = [(\langle \Delta n \rangle/\phi)_{\dot{\gamma}} - (\langle \Delta n \rangle/\phi)_{\dot{\varepsilon}}]^2. \quad (1)$$

Using the same interpolation procedure, multiple curves of $\langle \Delta n \rangle/\phi$ vs. $SF|\dot{\varepsilon}|$ are constructed upon increasing $SF$ by relatively small step as shown in Fig. 4(b). Analogously to eqn.1, for each $\langle \Delta n \rangle/\phi$ vs. $SF|\dot{\varepsilon}|$ curve we compute the Residuals$^2(|\dot{\gamma}|)$ as

$$\text{Residuals}^2(|\dot{\gamma}|) = [(\langle \Delta n \rangle/\phi)_{\dot{\gamma}} - (\langle \Delta n \rangle/\phi)_{SF|\dot{\varepsilon}|}]^2. \quad (2)$$
The results from the Residuals^2(|\dot{\gamma}|) are shown in Fig. S4(c) for 2 < SF < 25. For each SF, the residual sum of squares (RSS) is computed as

$$RSS(SF) = \sum_{i=1}^{n}(\text{Residuals}^2)_i,$$

(3)

where \( n \) is the number of |\dot{\gamma}| data points for each SF. For each SF, we then compute the average RSS as \( \langle RSS \rangle = RSS/n \) to account for the different number of data points between data sets. In Fig. S4(d) the \( \langle RSS \rangle \) vs. SF displays a clear minimum at SF = 9.5 (see red star), indicating that this is the scaling factor minimizing the \( \langle RSS \rangle \). Graphically, SF = 9.5 enables the best superimposition between the two curves, as shown in Fig. S4(e). Finally, according to eqn. 8 in the main text SF = (\( \alpha Tr_s \)), so that \( \alpha = 2.4 \) using \( Tr_s = 4.7 \).

**Figure S 4:** (a) Normalized birefringence, \langle \Delta n \rangle/\phi, for the L-WLNP dispersions at \( \phi = 66 \times 10^{-3} \) as a function of the shear and extensional rate (i.e., |\dot{\gamma}|, |\dot{\varepsilon}|, obtained in the SFC and OSCER device, respectively) with solid lines indicating the interpolated curves. (b) The interpolated curves for the \langle \Delta n \rangle/\phi vs. SF|\dot{\varepsilon}| upon increasing SF. (c) The Residuals^2(|\dot{\gamma}|) for several values of SF. (d) \langle RSS \rangle as a function of SF. The star symbol indicates the value of SF that minimizes the \langle RSS \rangle. (e) \langle \Delta n \rangle/\phi as a function of \|\dot{\gamma}\| and SF|\dot{\varepsilon}| using the value of SF that minimizes the \langle RSS \rangle (SF = 9.5).