Electronic Supplementary Material (ESI) for Soft Matter.

Shear-Induced Alignment of Block Copolymer Worms in Mineral Oil

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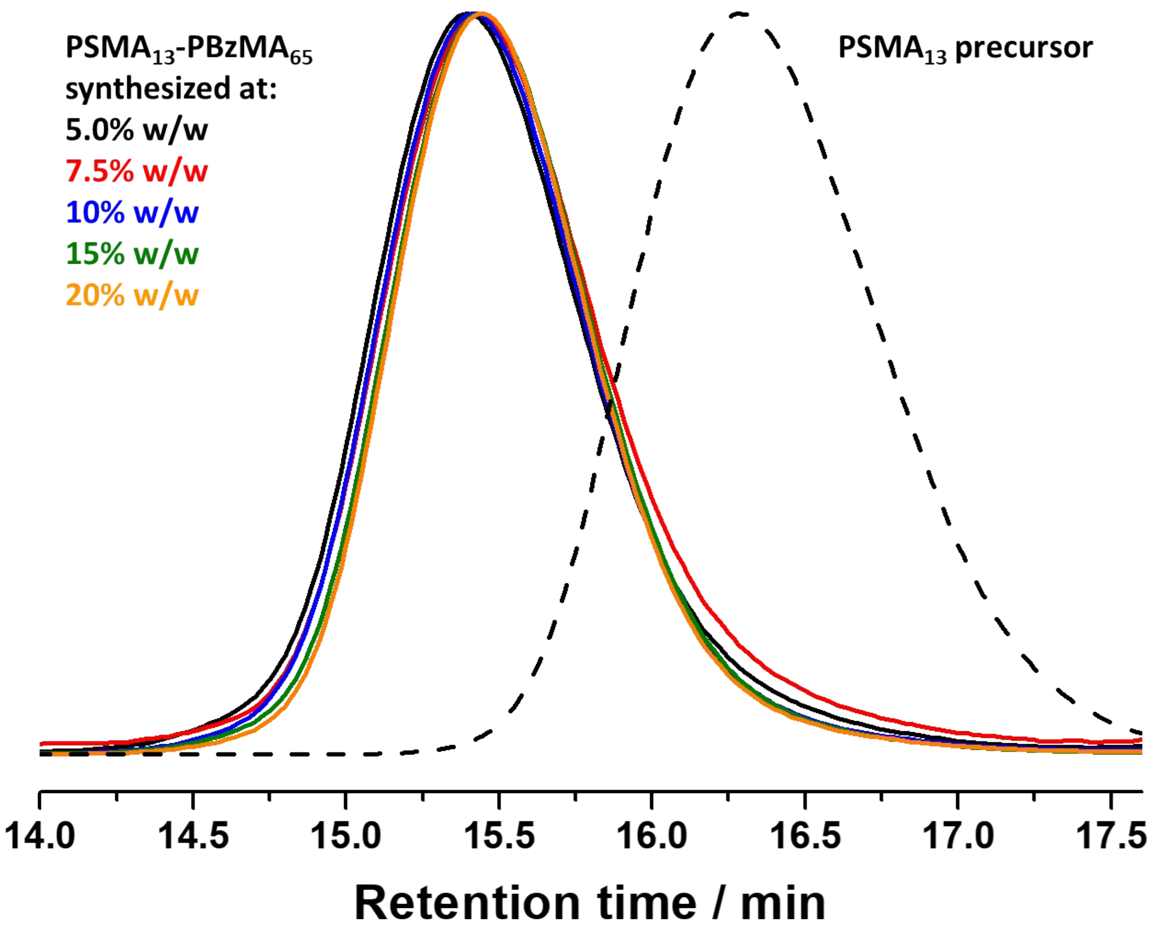

Figure S1. THF GPC curves obtained for targeted $PSMA_{13}$-$PBzMA_{65}$ diblock copolymer worms prepared via RAFT dispersion polymerization in mineral oil at various copolymer concentrations. The black dashed curve represents the $PSMA_{13}$ precursor and is displayed for reference.

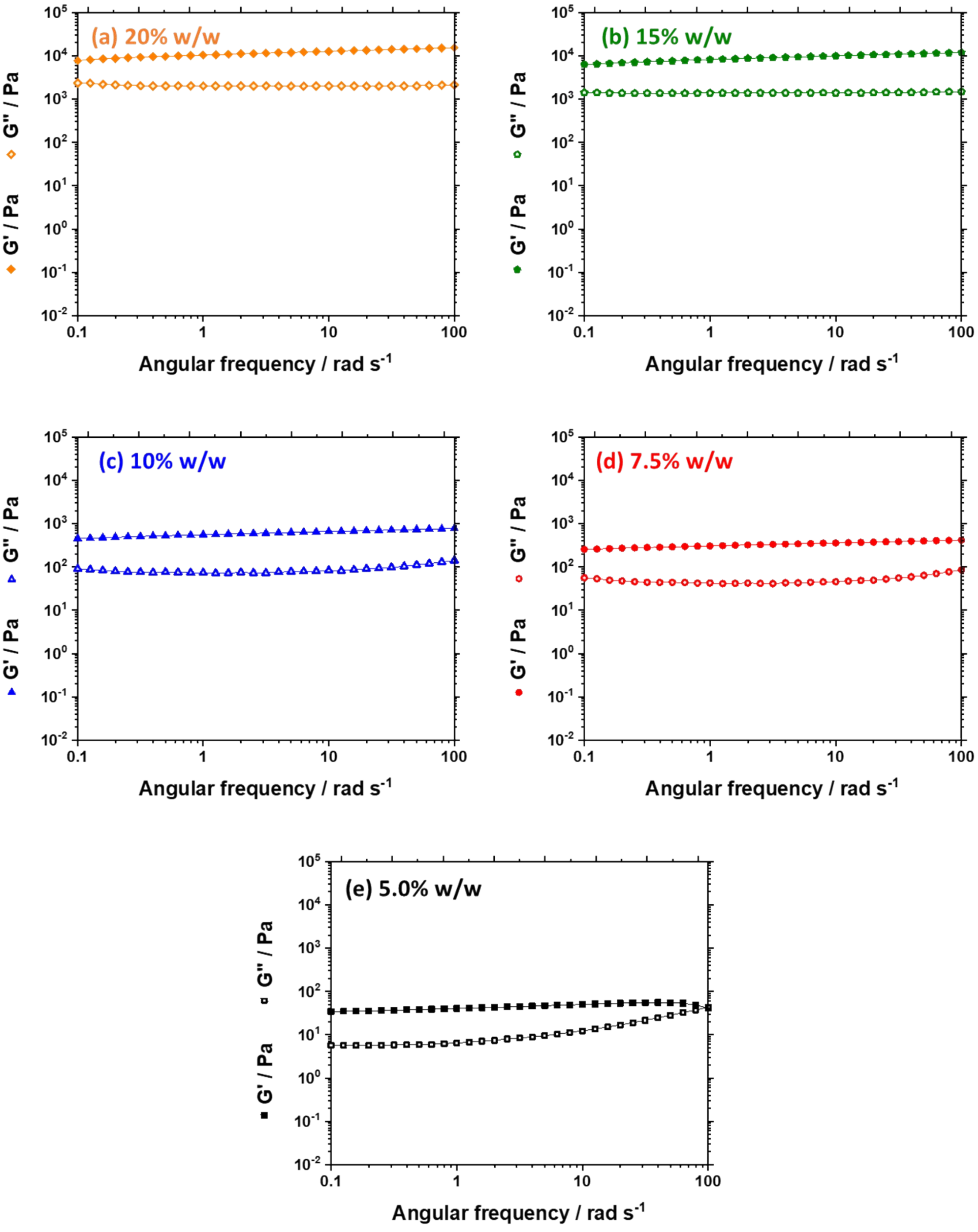

Figure S2. Variation of storage modulus (*G*') and loss modulus (*G*") with angular frequency for $PSMA_{13}$-$PBzMA_x$ worm gels (cone and plate geometry; 1.0% applied strain at 20 °C.

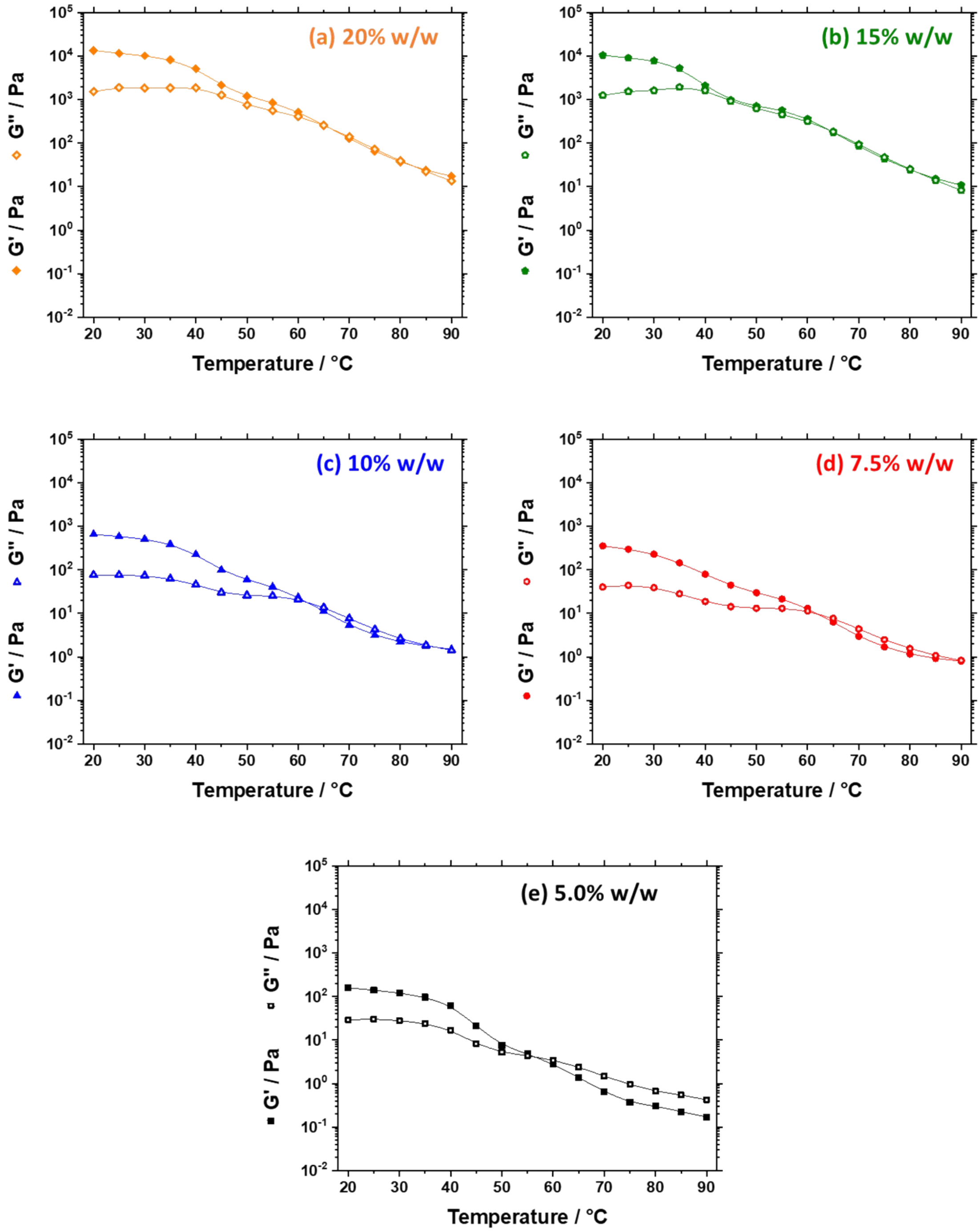

Figure S3. Variation of storage modulus (G') and loss modulus (G'') with temperature for $PSMA_{13}$-$PBzMA_x$ worm gels (cone and plate geometry; 1.0% applied strain at an angular frequency of 10 rad s^{-1}; data recorded at 5 °C intervals, with 5 min being allowed for thermal equilibration before each measurement).

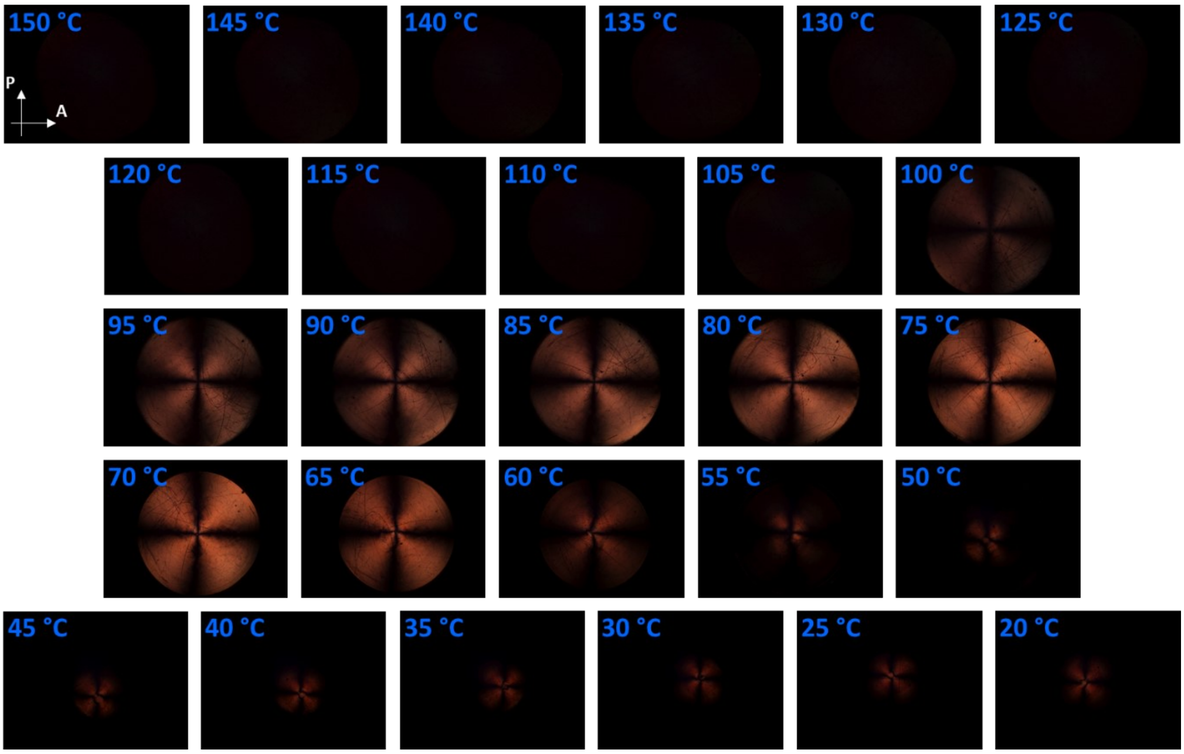

Figure S4. Polarized light images (PLIs) recorded for a 20% w/w dispersion of $PSMA_{13}$-$PBzMA_{64}$ nano-objects on cooling from 150 °C to 20 °C at 2 °C min^{-1} while subject to a constant maximum (sample edge) shear rate of 1 s^{-1}. Selected PLIs represent the sample birefringence observed at various temperatures (indicated by the blue labels). White arrows in the top left image indicate the planes of polarization for the polarizer (P) and the analyzer (A), crossed at 90°. A Maltese cross motif indicates shear-induced alignment of anisotropic objects, whereas its absence indicates either no the alignment or no anisotropic objects.

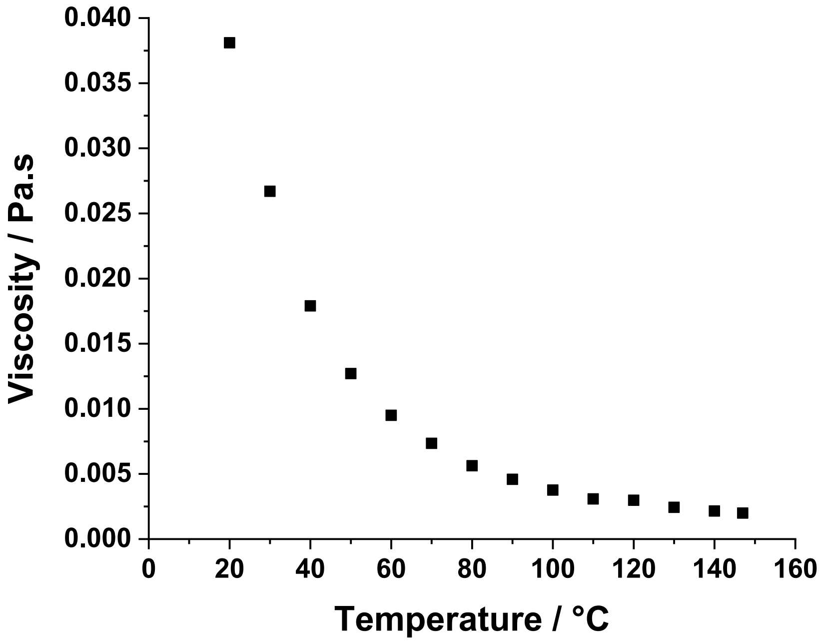

Figure S5. Viscosity-temperature profile obtained for mineral oil on heating from 20 °C to 147 °C, with each data point being collected after thermal equilibration.

Worm-like micelle SAXS model

Programming tools within the Irena SAS Igor Pro macros[1] were used to implement the structural model for SAXS analysis of worm-like micelles.

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

$$\frac{d\Sigma}{d\Omega}(q) = NS(q)\int_0^\infty \dots \int_0^\infty F(q,r_1,\dots,r_k)^2\Psi(r_1,\dots,r_k)dr_1,\dots,dr_k \qquad \text{(S1)}$$

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 nano-object structural morphology, $\Psi(r_1,\dots,r_k)$ is the distribution function, $S(q)$ is the structure factor and N is the number density of nano-objects per unit volume expressed as:

$$N = \frac{\varphi}{\int_0^\infty \dots \int_0^\infty V(r_1,\dots,r_k)\Psi(r_1,\dots,r_k)dr_1,\dots,dr_k} \qquad \text{(S2)}$$

where $V(r_1,\dots,r_k)$ is the nano-object volume and φ is the volume fraction of the nano-objects within the dispersion. It is assumed that $S(q)$ = 1 at the sufficiently low copolymer concentrations used in this study (1.0% w/w).

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

$$F_{wmic}(q,r_1) = N_w(r_1)^2\beta_s{}^2F_{sw}(q,r_1) + N_w(r_1)\beta + 2N_w(r_1)^2\beta_s\beta_cS_{sc}(q,r_1) \qquad \text{(S3)}$$

where r_1 is the worm micelle core radius, R_g is the radius of gyration of the coronal block (in this case, $PSMA_{13}$). The X-ray scattering length contrasts for the core and corona blocks 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_{PBzMA}= 10.38 x 10^{10} cm^{-2}), corona block (ξ_{PSMA}= 9.24 x 10^{10} cm^{-2}) and mineral oil solvent (ξ_{sol}= 7.63 x 10^{10} cm^{-2}), respectively. V_s and V_c are the volumes of the core block (V_{PBzMA}) and the corona block (V_{PSMA}), respectively. The self-correlation term for the worm micelle core is:

$$F_{sw}(q,r_1) = F_{worm}(q,L_w,b_w)A_{CSworm}^{\ 2}(qr_1) \tag{S4}$$

where

$$A_{CSworm}^{\ 2}(qr_1) = \left[2\frac{J_1(qr_1)}{qr_1}\right]^2 \tag{S5}$$

and J_1 is the first-order Bessel function of the first kind, and $F_{worm}(q,L_w,b_w)$ is a form factor for self-avoiding semi-flexible chains, where b_w is the worm Kuhn length and L_w is the mean worm contour length. A complete expression for the chain form factor can be found elsewhere.[2, 3] The self-correlation term of the corona block in Equation S3 is given by the Debye function: $F_c(q,R_g) = \frac{2\left[exp\left(-q^2R_g^{\ 2}\right) - 1 + q^2R_g^{\ 2}\right]}{q^4R_g^{\ 4}}$. The interference cross-term between the worm-like micelle core and the coronal stabilizer chains is taken to be: $S_{sc}(q,r_1) = \Psi(qR_g)A_{CSworm}(qr_1)J_0\left[q(r_1 + R_g)\right]F_{worm}(q,L_w,b_w)$, where $\Psi(qR_g) = \frac{1 - exp\left(-q^2R_g^{\ 2}\right)}{q^2R_g^{\ 2}}$ is the form factor amplitude of the corona chain and J_0 is the zero-order Bessel function of the first kind. The interference term between the worm corona chains is taken to be: $S_{cc}(q,r_1) = \Psi^2(qR_g)J_0^{\ 2}\left[q(r_1 + R_g)\right]F_{worm}(q,L_w,b_w)$. The aggregation number of the worm-like micelle, N_w, is given by:

$$N_w(r_1) = (1 - x_{sol})\frac{\pi r_1^{\ 2}L_w}{V_s} \tag{S6}$$

where x_{sol} is the volume fraction of solvent within the worm-like micelle cores (which was found to be close to zero in all cases). The possible presence of semi-spherical caps at both ends of each worm is neglected in this form factor.

A polydispersity for only one parameter, worm micelle core radius (r_1), is assumed for the micelle model, which is described by a Gaussian distribution. Thus, the polydispersity function in Equation S1 is given by:

$$\Psi(r_1) = \frac{1}{\sqrt{2\pi\sigma_{R_{wc}}{}^2}} exp\left(- \frac{(r_1 - R_{wc})^2}{2\sigma_{R_{wc}}{}^2} \right) \tag{S7}$$

where $\sigma_{R_{wc}}$ is the standard deviation for R_{wc}. In accordance with Equation S2, the number density per unit volume for the worm-like micelle model is expressed as:

$$N = \frac{\varphi}{\int_0^\infty V(r_1)\Psi(r_1)dr_1} \tag{S8}$$

where φ is the total volume fraction of copolymer in the worm-like micelles and $V(r_1)$ is the total volume of copolymer in a worm-like micelle $[V(r_1) = (V_s + V_c)N_w(r_1)]$.

References

1. J. Ilavsky and P. R. Jemian, 2009, **42**, 347-353.
2. J. S. Pedersen and M. C. Gerstenberg, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2003, **213**, 175-187.
3. J. S. Pedersen, C. Svaneborg, K. Almdal, I. W. Hamley and R. N. Young, *Macromolecules*, 2003, **36**, 416-433.