Supporting Information for:

Aqueous block copolymer worm gels can be readily reconstituted from freeze-dried worms

M. K. Kocik, O. O. Mykhaylyk and S. P. Armes*

¹³C NMR spectrum of 2-cyano-2-propyl phenethyl trithiocarbonate (PETTCCP)



Figure S1. Assigned 126 MHz 13 C NMR spectrum recorded for PETTCCP. The solvent peak (residual CH₂Cl₂) is also visible.

TEM studies



Figure S2. TEM images recorded for: (**a**) original worm gel ($PGMA_{57}$ -PHPMA₁₄₀), freeze-dried and redispersed in water resulting in an inhomogeneous slurry (image 3 of Figure 2 in the main text); the TEM grid was prepared immediately thereafter, (**b**) reconstituted gel obtained after molecular dissolution of the same diblock copolymer in methanol.



Figure S3. TEM images recorded for: (**a**) the original worm gel (PGMA₄₉-PHPMA₁₃₀), (**b**) reconstituted worm gels obtained after freeze-drying using the standard gel reconstitution protocol (PGMA₄₉-PHPMA₁₃₀-FD), (**c**) reconstituted worm gel after freezing the aqueous slurry at -25°C and warming up to 20°C (PGMA₄₉-PHPMA₁₃₀-FDF), (**d**) gel reconstituted after freeze-drying in room temperature (PGMA₄₉-PHPMA₁₃₀-RT), PGMA₄₉-PHPMA₁₃₀ gels reconstituted at various copolymer concentrations after freeze-drying: (**e**) 8.5%, (**f**) 12.5% or (**g**) 15%.

DLS studies

	$G_{49}H_{130}$	G ₄₉ H ₁₃₀ -FD	G ₄₉ H ₁₃₀
Т [°С]	in H ₂ O	in H₂O	in MeOH
25	133 (0.170)	126 (0.228)	
20	137 (0.187)	123 (0.226)	8** (0.181)
5	39 (0.237)	43 (0.310)	
	G ₅₇ H ₁₄₀	G ₅₇ H ₁₄₀ -FD	G ₅₇ H ₁₄₀
T [°C]	G ₅₇ H ₁₄₀ in H ₂ O	G ₅₇ H ₁₄₀ -FD in H ₂ O	G ₅₇ H ₁₄₀ in MeOH
T [°C] 25	G₅7H140 in H2O 113 (0.200)	G₅7H ₁₄₀ -FD in H₂O 101 (0.191)	G ₅₇ H ₁₄₀ in MeOH
T [°C] 25 20	G ₅₇ H ₁₄₀ in H ₂ O 113 (0.200) 106 (201)	G ₅₇ H ₁₄₀ -FD in H ₂ O 101 (0.191) 100 (0.177)	G ₅₇ H ₁₄₀ in MeOH 8** (0.062)

Table S1. DLS intensity-average diameters (and corresponding polydispersities, or PDI) obtained for 1.0 % aqueous dispersions of $PGMA_{49}$ -PHPMA₁₃₀ and $PGMA_{49}$ -PHPMA₁₃₀-FD (pH 3.6), 0.20% aqueous dispersions of $PGMA_{57}$ -PHPMA₁₄₀ and $PGMA_{57}$ -PHPMA₁₄₀ and $PGMA_{57}$ -PHPMA₁₄₀. FD and 10 % methanolic solutions of $PGMA_{49}$ -PHPMA₁₃₀ and $PGMA_{57}$ -PHPMA₁₄₀. ** Unimers are present in these methanolic solutions, but the reported DLS size is not considered to be reliable at this copolymer concentration. The PGMA and PHPMA blocks are herein abbreviated to G and H.

DLS uses three statistical methods¹ (see below) to calculate the mean particle diameter.

Size/Intensity - "The size classes and the associated mean relative percentage of particles in each class based on the intensity of light scattered".¹ Statistical analysis is biased towards larger particles in the size distribution as they scatter much more light than smaller particles.

Size/Volume – "The size classes and the associated mean relative percentage of particles in each class based on the volume occupied".¹ This is considered the most accurate method to determine the particle polydispersity, hence this parameter was used in the present study.

Size/Number – "The size classes and the associated mean relative percentage of particles in each class based on the numbers of particles".¹ Statistical analysis is biased towards the smaller particles in the size distribution.



Figure S4. DLS particle size distributions recorded for a 0.20 % aqueous dispersion of PGMA₅₇-PHPMA₁₄₀-FD at 25, 20 or 5°C and for a 10% methanol solution of PGMA₅₇-PHPMA₁₄₀-FD at 20°C. PSD calculated by intensity (**a**), volume (**b**) or number (**c**).

*** Sample was equilibrated for 1 h at 5 °C.

Rheology Studies



Figure S5. Variation of G' and G'' with temperature from 4°C to 35°C (heating cycle) or from 35°C to 4°C (cooling cycle) at a fixed frequency of 1.0 rad s⁻¹ and 1.0 % strain for: (**a**) the original PGMA₄₉-PHPMA₁₃₀ and (**c**) PGMA₅₇-PHPMA₁₄₀ worm gels (denoted $G_{49}H_{130}$ and $G_{57}H_{140}$) and the corresponding reconstituted worm gels obtained after freeze-drying (**b**) PGMA₄₉-PHPMA₁₃₀-FD and (**d**) PGMA₅₇-PHPMA₁₄₀-FD (denoted $G_{49}H_{130}$ -FD and $G_{57}H_{140}$ -FD).



Figure S6. Rheology data: (**a**) temperature sweep for adjusted frequency = 1 rad/s and strain = 1% for freeze-dried gels reconstituted by varying the gel formation protocol: (i) original worm gel (PGMA₄₉-PHPMA₁₃₀), (ii) gel reconstituted after freeze-drying at room temperature (PGMA₄₉-PHPMA₁₃₀-RT), (iii) reconstituted worm gels obtained after freeze-drying using the standard gel reconstitution protocol (PGMA₄₉-PHPMA₁₃₀-FD), (iv) reconstituted worm gel after freezing the aqueous slurry at -25°C and warming up to room temperature (PGMA₄₉-PHPMA₁₃₀-FDF); (**b**) frequency sweep for adjusted strain = 1% at 20°C, for (i) original worm gel (PGMA₅₇-PHPMA₁₄₀), (ii) reconstituted worm gels obtained after freeze-drying using the standard gel reconstitution protocol (PGMA₅₇-PHPMA₁₄₀), (ii) reconstituted worm gels obtained after freeze-drying using the standard gel reconstitution protocol (PGMA₅₇-PHPMA₁₄₀-FD) and (iii) reconstituted gel after molecular dissolution in methanol (PGMA₅₇-PHPMA₁₄₀-CH₃OH). PGMA and PHPMA are herein abbreviated to G and H.

Assessment of gel transparency via visible absorption spectroscopy



Figure S7. Visible absorption spectra recorded for: (**a**) (i) original worm gel (PGMA₄₉-PHPMA₁₃₀, black curve), (ii) gel reconstituted after freeze drying at room temperature (PGMA₄₉-PHPMA₁₃₀-RT, red curve), (iii) reconstituted worm gels obtained after freeze-drying using the standard gel reconstitution protocol (PGMA₄₉-PHPMA₁₃₀-FD, blue curve), (iv) reconstituted worm gel after freezing the aqueous slurry at -25°C and warming up to room temperature (PGMA₄₉-PHPMA₁₃₀-FDF, green curve). (**b**) Visible absorption spectra recorded for: (i) original worm gel (PGMA₅₇-PHPMA₁₄₀, black curve), (ii) reconstituted worm gels obtained after freeze-drying using the standard gel reconstitution protocol (PGMA₅₇-PHPMA₁₄₀-FD, blue curve), (iii) reconstituted worm gel after freezing the aqueous slurry at -25°C and warming up to 20°C (PGMA₅₇-PHPMA₁₄₀-FDF, green curve), (iv) reconstituted gel after molecular dissolution in methanol (PGMA₅₇-PHPMA₁₄₀-CH₃OH, red curve). PGMA and PHPMA are herein abbreviated to G and H.

Visible absorption spectra indicate reduced transparency (i.e. higher absorbance) for the reconstituted worm gel obtained at room temperature (PGMA₄₉-PHPMA₁₃₀-RT) and greater transparency for the PGMA₄₉-PHPMA₁₃₀-FD and PGMA₄₉-PHPMA₁₃₀-FDF worm gels compared to the original worm gel (see Figure S7a).

SAXS analysis

SAXS patterns for molecularly dissolved chains (unimers) was fitted by a scattering intensity equation for a Gaussian polymer chain:

$$I(q) = \phi(\Delta\xi)^2 V_{mol} F_{mol}(q)$$
(S1)

where \emptyset is the volume fraction of polymer in solution, $\Delta \xi$ is the averaged contrast scattering length density of the copolymer, V_{mol} is the total volume of the molecule. The form factor of a Gaussian polymer chain is: ²

$$F_{mol}(q) = \left[\frac{1}{\nu U^{1/(2\nu)}} \gamma\left(\frac{1}{2\nu}, U\right) - \frac{1}{\nu U^{1/\nu}} \gamma\left(\frac{1}{\nu}, U\right)\right]$$
(S2)

with the modified variable $U = (2\nu+1)(2\nu+2)\frac{q^2R_g^2}{6}$, where ν is the excluded volume parameter and $\gamma(s,x) = \int_0^x t^{s-1} \exp(-t)dt$ is the lower incomplete gamma function. Thus, two fitting parameters are used for $F_{mol}(q)$. Programming tools of the Irena SAS Igor Pro macros ³ was used to implement the model fitting. A fit to the SAXS pattern of PGMA₅₇-PHPMA₁₄₀ aqueous solution at -2 °C produced $\nu = 0.46$ and $R_g = 6.0$ nm (Figure 4a in the main text). The ν parameter is slightly less than 0.5 corresponding to a "theta" solvent condition. However, the R_g value is significantly different from an expected value for a single PGMA₅₇-PHPMA₁₄₀ molecule. It can be estimated by using the poly(methyl methacrylate) (PMMA) Kuhn length (b = 1.53 nm) and the ν value that the radius of gyration of a single PGMA₅₇-PHPMA₁₄₀ molecule should be about 3.2 nm [$R_g^2 = \frac{b^{2(1-\nu)}L_{mol}^{2\nu}}{(2\nu+1)(2\nu+2)}$, where $L_{mol} = (57 + 140) \times$

0.255 nm = 50.3 nm is the total contour length of the molecule assuming that the blocks comprising the molecules have the same projected contour length of their monomers as the PMMA]. Such a significant difference between the estimated value and the measured value (3.2 nm vs. 6.0 nm) suggests that the sphere micelles in aqueous solution do not disintegrate into single molecules upon cooling to -2 °C and the copolymers at these conditions either remain assembled in bigger objects or rather exist as a mixture of spherical micelles and unimers as found by DLS measurements at 5 °C (Figure 4b or Figure S4). This conclusion is supported by a simple experiment. It was found by DLS and SAXS that a diblock copolymer solution in methanol, which is a better solvent for the PHPMA block than cold water, has a hydrodynamic radius of around 4 nm (Figure 4b, see comment in the footnotes for Table S1) and a radius of gyration, R_g of 2.6 nm (Figure 4a, red squares),

respectively. These values are comparable to the R_g of 3.2 nm estimated from SAXS analysis and suggest that the copolymer is fully dissolved in methanol. The absolute scale of the SAXS intensity measurements (Figure 4a) provides an opportunity for an additional estimation. If the copolymer molecules is fully dissolved than the volume of a scattering object should be equal to the volume of a molecule (V_{mol} = 39.3 nm³ for the studied copolymer, which is a sum of the block volumes; the volume of each block comprising the copolymer, V_{PHPMA} = 27.7 nm³ and V_{PGMA} = 11.6 nm³, can be obtained from $V = \frac{M_w}{N_{e} O}$ by using

the following mass densities, $\rho_{PHPMA} = 1.21 \text{ g cm}^{-3}$ and $\rho_{PGMA} = 1.31 \text{ g cm}^{-3}$, measured by helium pycnometry). According to Eq. (S1) SAXS intensity of the 10 wt % copolymer methanol solution at low q should be about 3.74 cm⁻¹ [$I(0) = 0.066 \times (3.8 \times 10^{10} \text{ cm}^{-2})^2 \times$ 39.3 nm³, where $\phi = 0.066$ corresponds to the 10 wt % copolymer solution in methanol and $\Delta \xi = 3.8 \times 10^{10} \text{ cm}^{-2}$ is the average scattering contrast of the PGMA₅₇-PHPMA₁₄₀ copolymer in this solvent]. The $\Delta \xi$ is obtained as a difference between the average scattering length density of the copolymer

 $\left(\frac{V_{PHPMA}\xi_{PHPMA} + V_{PGMA}\xi_{PGMA}}{V_{mol}}\right)$, where $\xi_{PHPMA} = 11.11 \times 10^{-10} \text{ cm}^{-2}$ and $\xi_{PGMA} = 11.94 \times 10^{-10} \text{ cm}^{-2}$) and the scattering length density of the solvent ($\xi_{MeOH} = 7.55 \times 10^{-10} \text{ cm}^{-2}$).

The experimental SAXS intensity at low q is about 3.3 cm⁻¹ (Figure 4a, red squares); this corresponding to 9 wt % copolymer solution, which correlates well with the estimated I(0) value of 3.74 cm⁻¹.

References

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