

Supplementary Information

Shaping block copolymer micelles by supramolecular polymerization: Making 'Tubisomes'

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1. NMR spectra of the investigated compounds

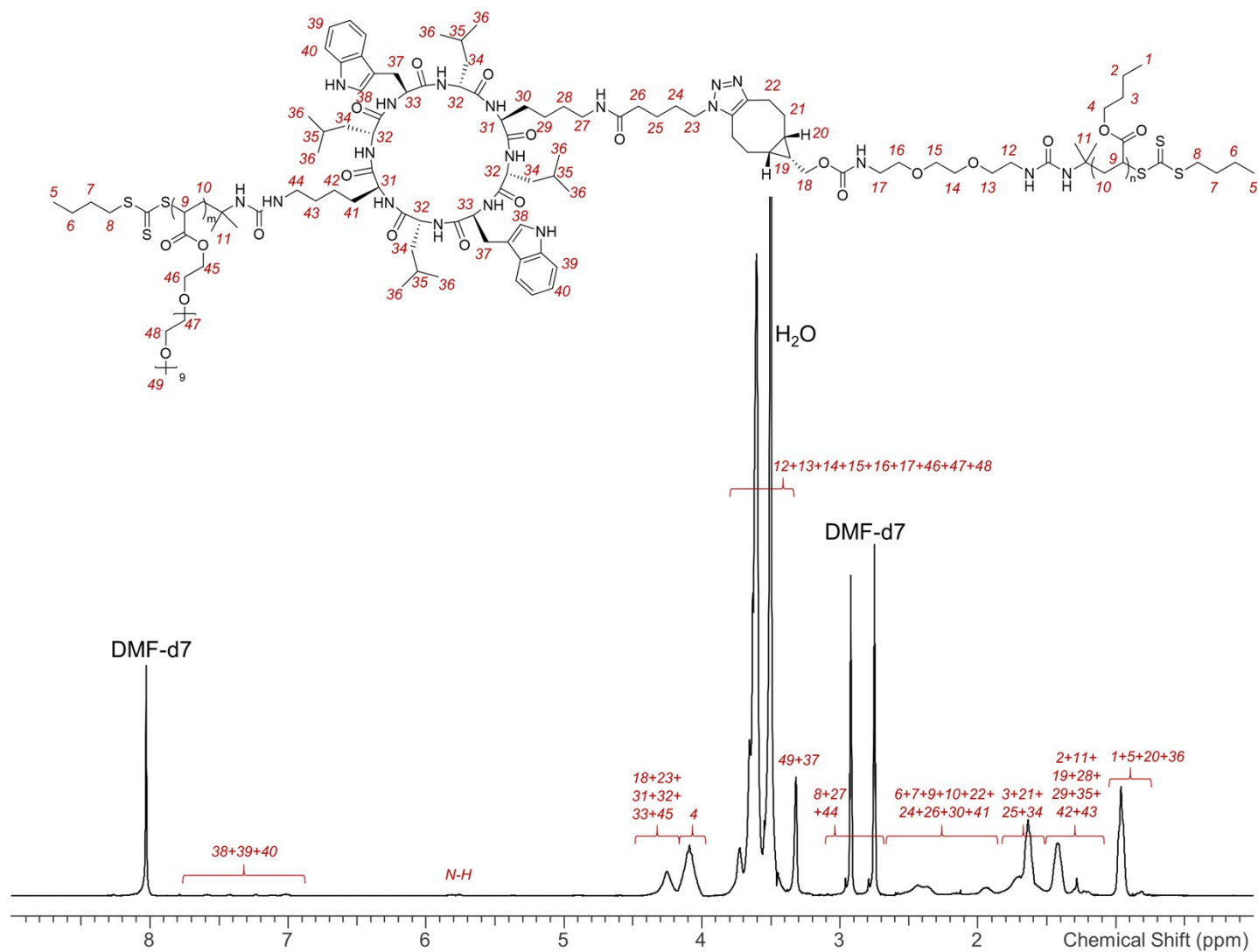


Figure S1. NMR spectrum of PBA₅₃-CP-PPEGA₂₆.

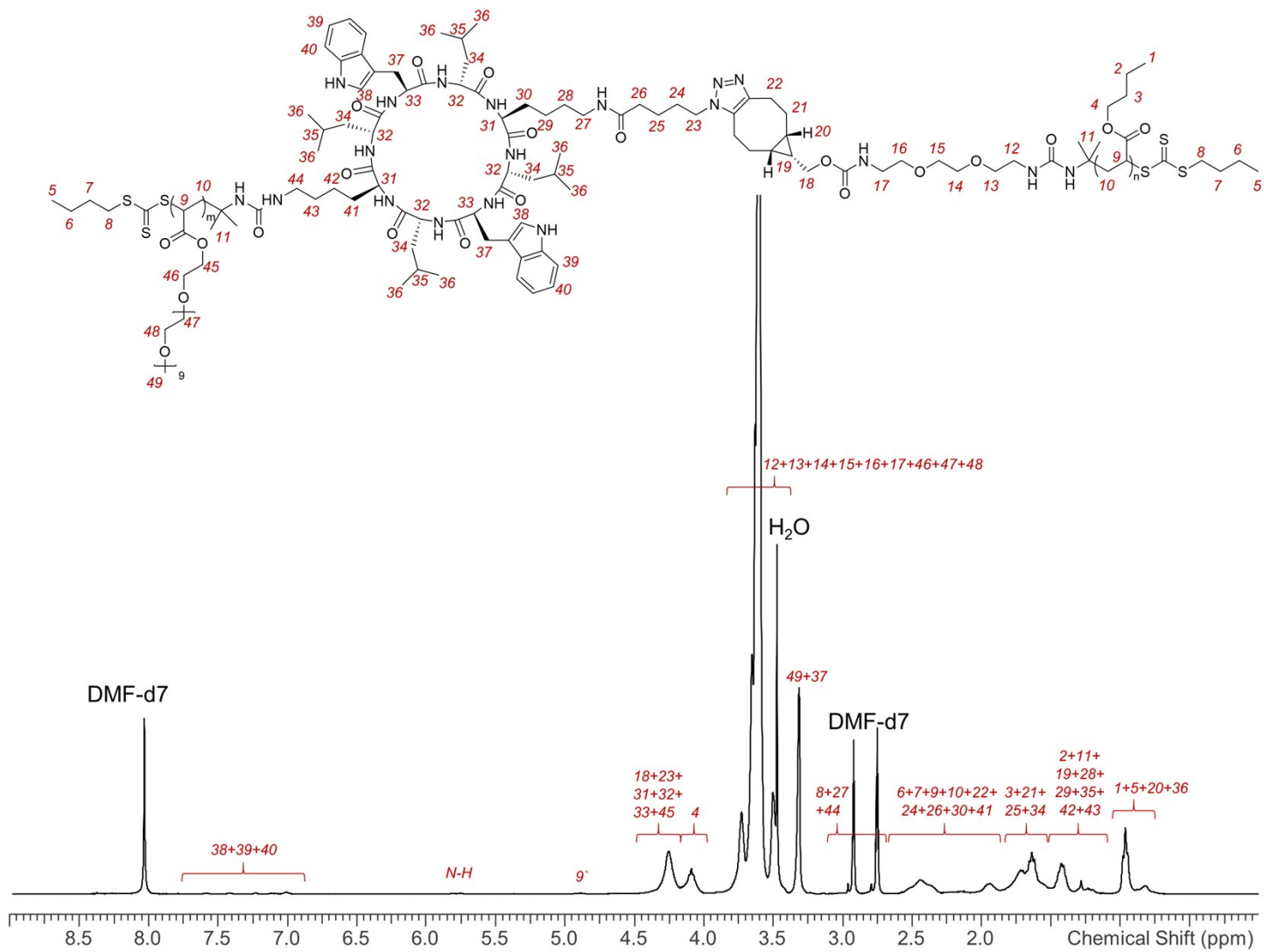


Figure S2. NMR spectrum of PBA₂₃-CP-PPEGA₂₆.

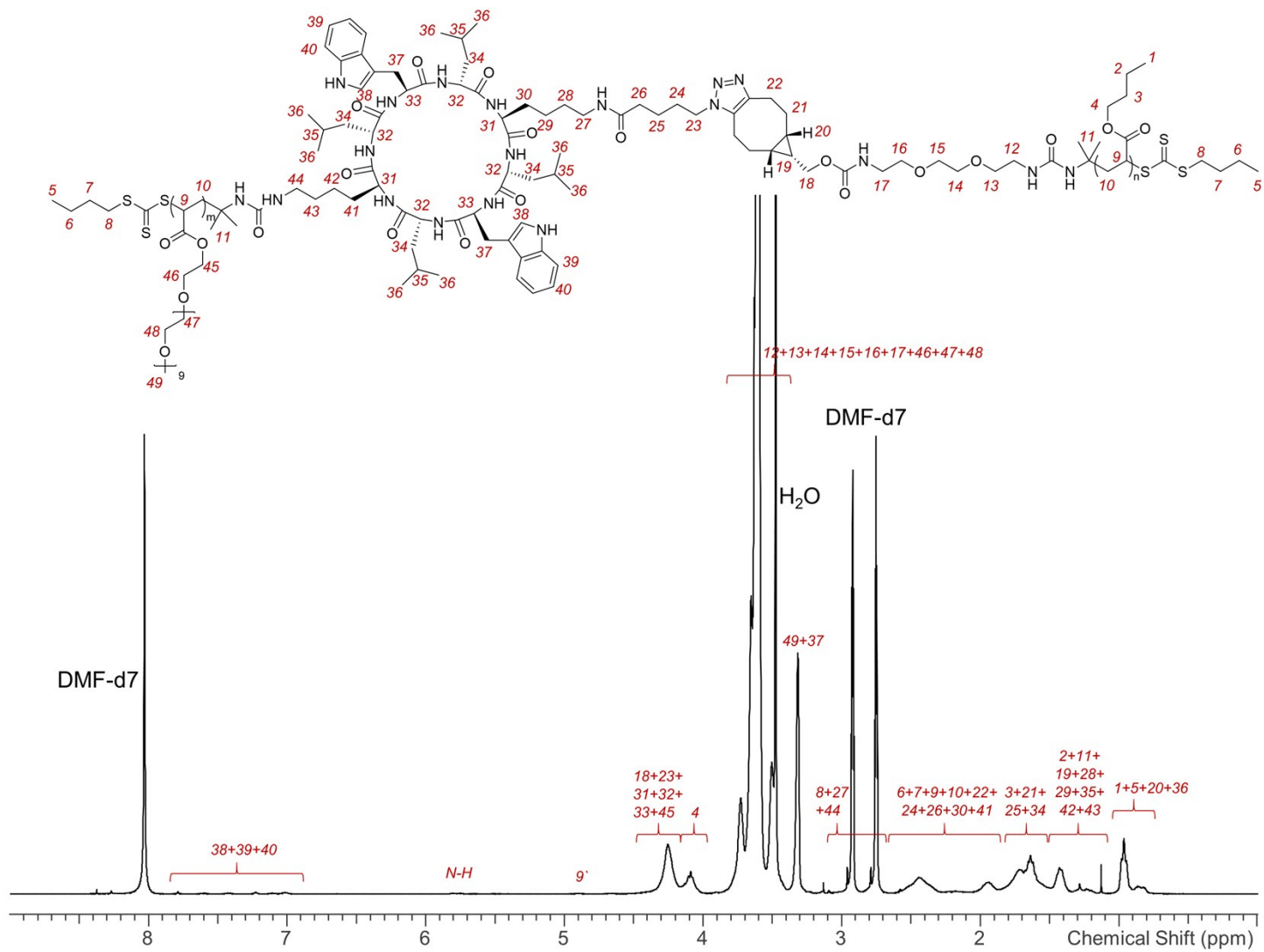


Figure S3. NMR spectrum of PBA₂₃-CP-PPEGA₄₅.

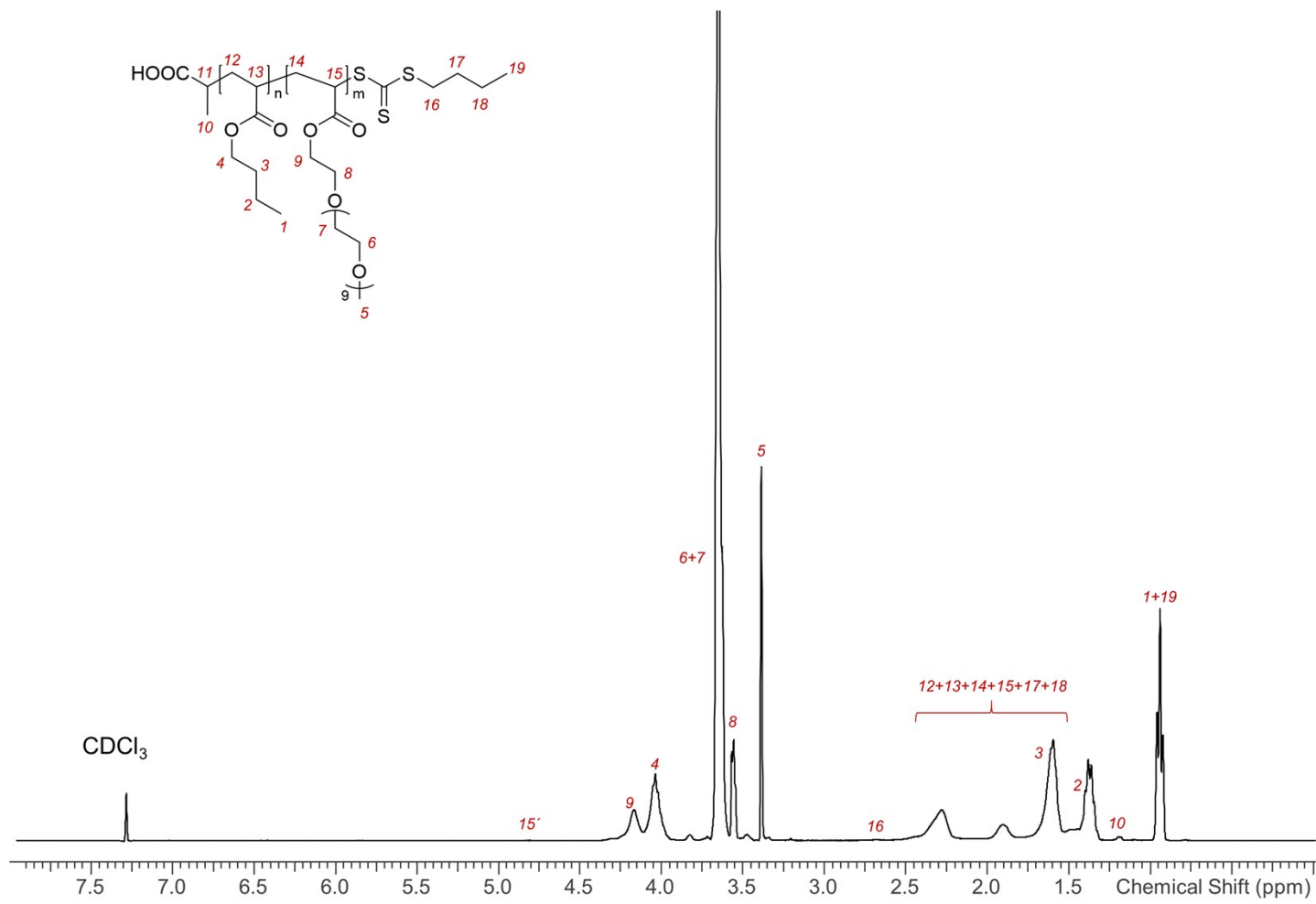


Figure S4. NMR spectrum of PBA₅₃-*b*-PPEGA₂₇.

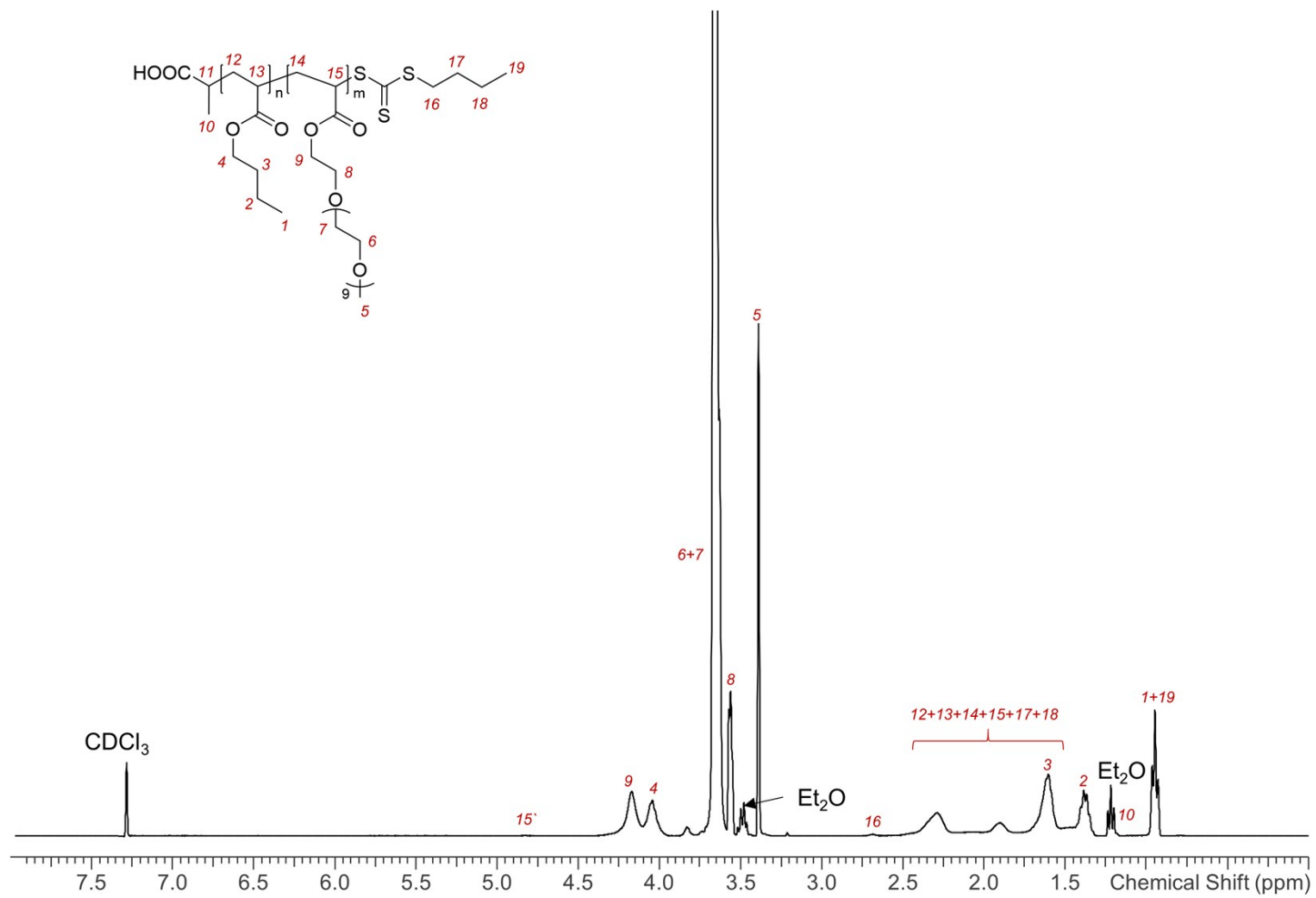


Figure S5. NMR spectrum of PBA₂₇-*b*-PPEGA₂₈.

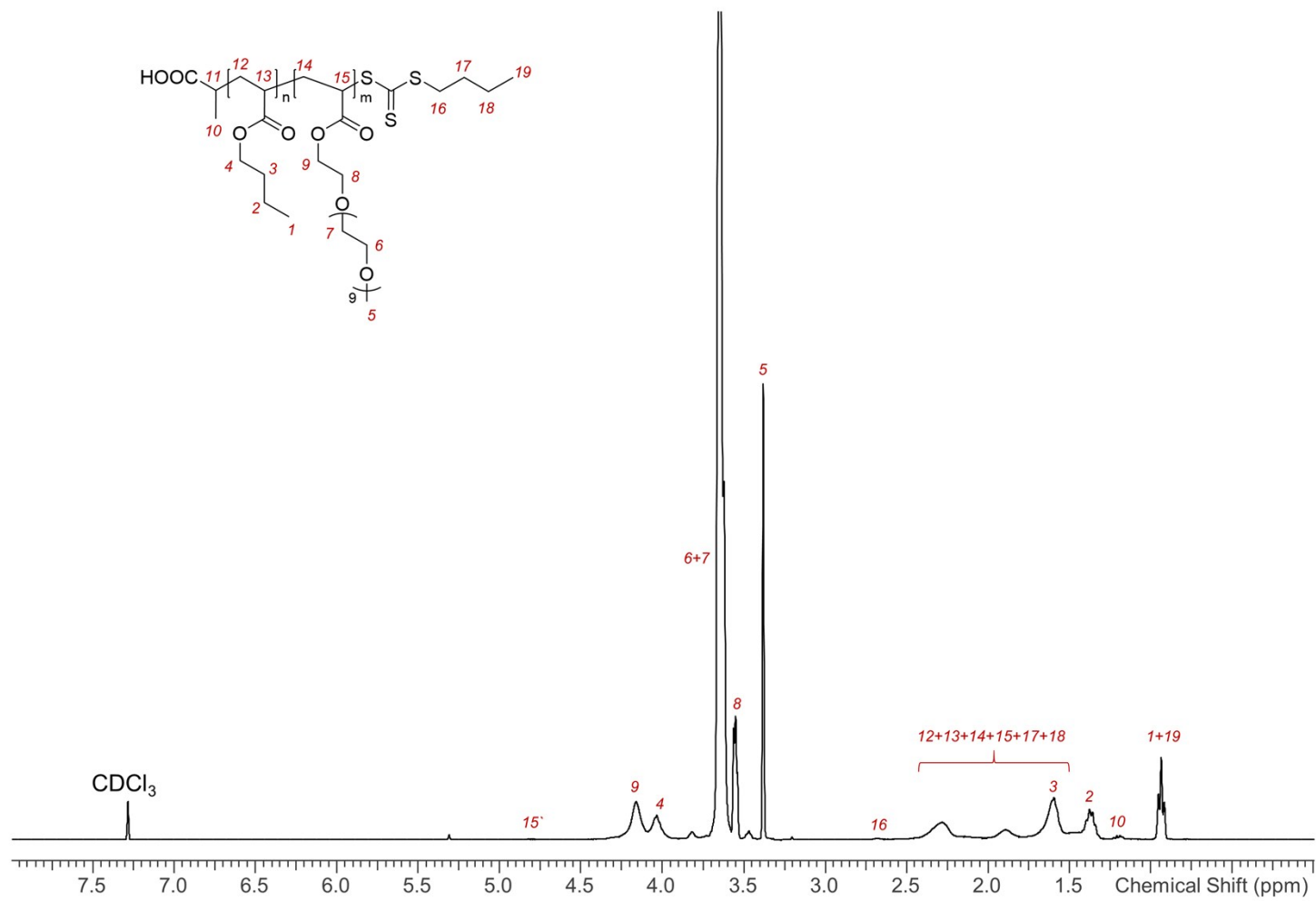


Figure S6. NMR spectrum of PBA₂₇-*b*-PPEGA₄₅.

2. Kinetics of the coupling reaction

The progress of the coupling reaction for PBA₅₃-CP-PPEGA₁₆ was monitored by size exclusion chromatography. Samples of the reaction mixture were taken after 24 h, 48 h, and 72 h. The reaction was finally stopped after 168 h (1 week) as no further conversion could be detected.

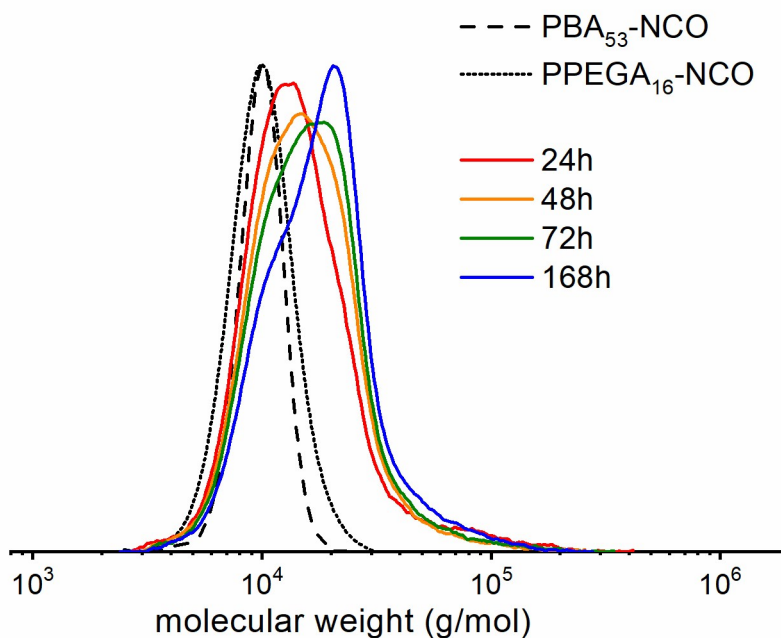


Figure S7. SEC traces of the starting materials (PBA and PPEGA) and samples taken from the conjugation of sample PBA₅₃-CP-PPEGA₁₆.

3. SEC traces of the block copolymers

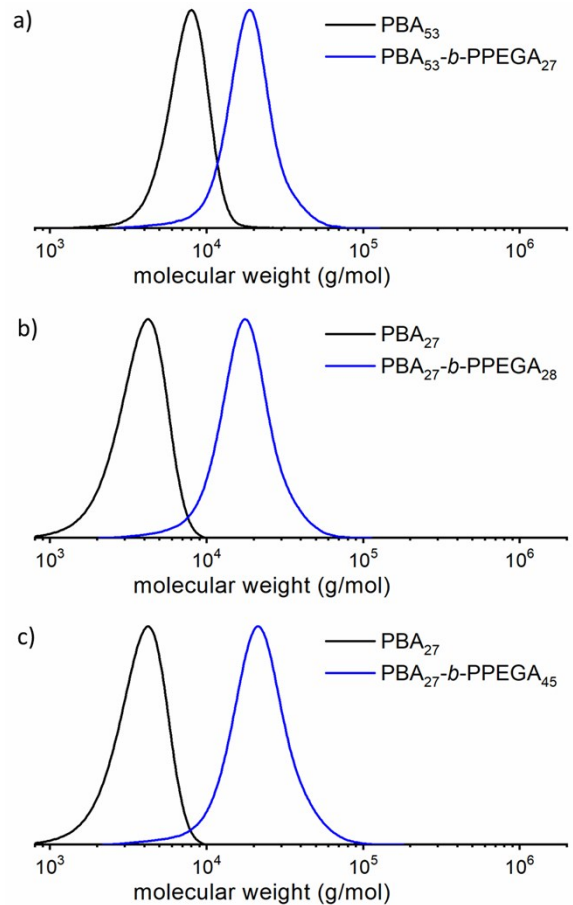


Figure S8. SEC traces of the first blocks (PBA) and the final block copolymers for the samples PBA₅₃-*b*-PPEGA₂₇ (a), PBA₂₇-*b*-PPEGA₂₈ (b), and PBA₂₇-*b*-PPEGA₄₅ (c).

4. Neutron (SANS) and light scattering (SLS) experiments on solutions in water

- Preparation of the solutions for SANS and SLS measurements

All samples were prepared by dilution of a stock solution (100 mg/ml) in DMSO-*d* with D₂O to give a final concentration of 1 mg/ml. The addition of D₂O has to be done very slowly, in particular at the beginning (first 10% of D₂O addition), to reach equilibrium in the system. Any additional aggregates formed during this process were dispersed by sonication for 20 s using a sonifier (Branson, 400W).

- Static Light Scattering (SLS)

The Rayleigh ratio, R , of the solution was determined following equation (1).

$$R = \frac{I_{\text{solution}}(\theta) - I_{\text{solvent}}(\theta)}{I_{\text{toluene}}(\theta)} \times R_{\text{toluene}}$$

(equation 1)

with I_{solution} , I_{solvent} and I_{toluene} the average intensities scattered respectively by the solution, the solvent and the reference (toluene) and $R_{\text{toluene}} = 1.35 \times 10^{-5} \text{ cm}^{-1}$ the Rayleigh ratio of toluene for a wavelength $\lambda = 632.8 \text{ nm}$.

At a given concentration C , R is related to the apparent weight average molecular weight of the scatterers, M_a , and to the structure factor, $P(q)$, which depends on the scattering wave vector according to equations (2) and (3).¹ Note that the apparent molecular weight M_a corresponds to the true molecular weight M_w only in very dilute solutions where the interactions between the scatterers can be neglected. At higher concentration, interactions cause M_a to differ strongly from M_w .²

$$R = K.C.M_a.P(q) \quad (\text{equation 2})$$

with C the polymer concentration in g/L and $P(q)$ the form factor. When $q \cdot R_g < 1$ is verified, $P(q)$ is negligible. K is a constant which, for SLS, is given by:

$$K = \frac{4\pi^2 n_s^2}{\lambda_0^4 \times N_A} \times \left(\frac{\partial n}{\partial C} \right)^2 \times \left(\frac{n_{toluene}}{n_{solvent}} \right)^2 \quad (\text{equation 3})$$

where N_A is Avogadro's number, $n_{solvent} = 1.333$ (water) and $n_{toluene} = 1.496$ the respective refractive indexes of the solvent and of toluene.

For $q < 18800000 \text{ m}^{-1}$, the scatterers were small, so that their apparent radius of gyration R_g verified $q \cdot R_g < 1$. In this case, equation (2) could be approximated to equation (4) corresponding to the Zimm approximation.² Plotting KC/R_0 as a function of q^2 for each concentration yielded the apparent radius of gyration R_g of the scatterers as well as their apparent molecular weight extrapolated to zero angle, M_a . Accurate determination of R_g was possible since $R_g > 20 \text{ nm}$ and

$$q \cdot R_g < 1.$$

$$\frac{KC}{R} = \frac{I}{M_a \cdot S(q)} = \frac{I}{M_a} \cdot \left[1 + \frac{q^2 \cdot R_g^2}{3} \right] \quad (\text{equation 4})$$

- *Small angle neutron scattering (SANS)*

Small angle neutron scattering was carried out on the Sans2d small-angle diffractometer at the ISIS Pulsed Neutron Source (STFC Rutherford Appleton Laboratory, Didcot, U.K.).³ A collimation length of 4 m and incident wavelength range of 1.75 – 16.5 Å was employed. Data were measured simultaneously on two 1 m² detectors to give a Q-range of 0.0045 – 1.00 Å⁻¹. The small-angle detector was positioned 4 m from the sample and offset vertically 60 mm and sideways 100 mm. The wide-angle detector was positioned 2.4 m from the sample, offset sideways by 980 mm and rotated to face the sample. Q is defined as:

$$Q = \frac{4\pi \sin \frac{\theta}{2}}{\lambda} \quad (\text{equation 5})$$

where θ is the scattered angle and λ is the incident neutron wavelength. The beam diameter was 8 mm. Each raw scattering data set was corrected for the detector efficiencies, sample transmission and background scattering and converted to scattering cross-section data ($\partial\Sigma/\partial\Omega$ vs. Q) using the instrument-specific software.⁴ These data were placed on an absolute scale (cm^{-1}) using the scattering from a standard sample (a solid blend of hydrogenous and perdeuterated polystyrene) in accordance with established procedures.⁵ In order to compare SANS and light scattering data directly, we have expressed the SANS results in terms of M_a using equation 2. For SANS the constant K is given by:

$$K_{SANS} = \frac{1}{N_A} \times \left(\frac{\rho_{solute} - \rho_{solvent}}{d} \right)^2 \quad (\text{equation 6})$$

where d is the density of the solution. ρ_{solute} is the scattering length density for the polymer and has been computed according to its chemical structure.

The obtained reduced data was analyzed with the open access software SASfit.⁶ For all conjugates with the cyclic peptide and the samples PBA₂₇-*b*-PPEGA₂₈ and PBA₅₃-*b*-PPEGA₂₈ a form factor of a diblock copolymer micelle with rod-like core was applied.⁷ The best fit for the block copolymer PBA₂₇-*b*-PPEGA₄₅ was obtained using a form factor of a micelle with a spherical core.⁷

Form factor for a micelle with a rod-like core

The best model used to fit the SANS data for the samples PBA₂₃-CP-PPEGA₄₅, PBA₂₃-CP-PPEGA₂₆, PBA₅₃-CP-PPEGA₂₆, PBA₂₇-*b*-PPEGA₂₈, and PBA₅₃-*b*-PPEGA₂₈ in D₂O was that of a hairy rod-like micelle.

$$P(q) = N^2\beta_s^2 F_{s(q)} + N\beta_c^2 F_{c(q)} + 2N^2\beta_s\beta_c S_{sc(q)} + N(N-1)\beta_c^2 S_{cc(q)} \quad (\text{equation 7})$$

where N is the aggregation number, $\beta_s = V_s(\rho_s - \rho_{solv})$ and $\beta_c = V_c(\rho_c - \rho_{solv})$ are the total excess scattering lengths of a block in the cylindrical core and in the corona, respectively. V_s and V_c are

the volumes of a block in the core and in the corona, respectively. ρ_s and ρ_c are the corresponding scattering length densities and ρ_{solv} is the scattering length density of the surrounding solvent.

$$F_{s(q,R,L)} = F_{cs(q,R)} F_{L(q,L)} \text{ where } F_{cs(q,R)} = \left[\frac{2B_1(qR)}{qR} \right]^2, \quad F_{L(q,L)} = 2 \frac{Si(qL)}{qL} - \frac{4 \sin^2\left(\frac{qL}{2}\right)}{q^2 L^2} \quad B_1 \text{ is the first order}$$

Bessel function and
$$Si(x) = \int_0^x \frac{\sin t}{t} dt$$

$$F_{c(q)} = \frac{2[\exp(-q^2 R_g^2) - 1 + q^2 R_g^2]}{q^4 R_g^4}$$

$$S_{sc(q)} = \psi(qR_g) \frac{2B_1(qR)}{qR} B_0[q(R + dR_g)] F_{L(q,L)} \text{ where } \psi(qR_g) = \frac{1 - \exp(-qR_g)}{qR_g}, \quad R_g \text{ is the gyration}$$

radius of the block of the corona, and B_0 is the zeroth order Bessel function.

$$S_{cc(q)} = \psi(qR_g)^2 B_0[q(R + dR_g)]^2 F_{L(q,L)}.$$

The scattering length densities were calculated according to the respective chemical structure.

The fit was performed with R , L , R_g , N_{agg} and N as adjustable parameter. The values afforded by the fit are gathered in Table S1 in the following.

Table S1. Fitting parameters for all cylindrical samples using a form factor of a micelle with a rod-like core

parameter	PBA ₂₃ -CP- PPEGA ₄₅	PBA ₂₃ -CP- PPEGA ₂₆	PBA ₅₃ -CP- PPEGA ₂₆	PBA ₂₇ - <i>b</i> - PPEGA ₂₈	PBA ₅₃ - <i>b</i> - PPEGA ₂₈	
R _{core} (Å)	76.5	77.8	95.3	22.1	35.5	Fitted
L _{core} (Å)	2595.9	2487.8	3930.4	273.9	1508.7	
R _{g, corona} ^a (Å)	36.0	30.3	28.8	19.8	20.4	
N _{agg} ^b	6605	6551	8559	74.3	567.3	
N	1.13 × 10 ⁻⁴	2.79 × 10 ⁻⁴	1.33 × 10 ⁻⁴	2.05 × 10 ⁻²	3.18 × 10 ⁻³	
V _{core} ^c (Å ³)	7223.1	7223.1	13097.1	5677.1	10511.9	Calculated
V _{corona} ^c (Å ³)	33160.9	19319.9	19319.9	19941.0	19941.0	
ρ _{core} ^d (cm ⁻¹)	8.84 × 10 ⁻⁷	8.84 × 10 ⁻⁷	7.91 × 10 ⁻⁷	6.76 × 10 ⁻⁷	6.85 × 10 ⁻⁷	
ρ _{corona} ^d (cm ⁻¹)	7.25 × 10 ⁻⁷	7.20 × 10 ⁻⁷	7.20 × 10 ⁻⁷	7.20 × 10 ⁻⁷	7.20 × 10 ⁻⁷	
ρ _{solvent} ^d (cm ⁻¹)	6.39 × 10 ⁻⁶	6.39 × 10 ⁻⁶	6.39 × 10 ⁻⁶	6.39 × 10 ⁻⁶	6.39 × 10 ⁻⁶	
d	1.1 ^e	1.1 ^e	1.1 ^e	0.8 ^f	0.8 ^f	
Background subtracted	9.0 × 10 ⁻⁴	1.5 × 10 ⁻³	8.0 × 10 ⁻⁴	1.0 × 10 ⁻³	1.4 × 10 ⁻³	

^a Radius of gyration (R_g) of a single chain in the corona;

^b The number of aggregation (N_{agg}) was calculated from the volume of the whole core divided by the volume of the core of a single unit;

^c The Volume of a single polymer chain in the core (PBA+CP: V_{core}) or corona (PPEGA: V_{corona}) was estimated from the Mn, divided by the Avogadro constant and assuming a density of 1.1 g/cm³;

^d The scattering lengths density (SLD) of the materials was calculated using the calculator given in SASfit;

^e d represents a penetration factor for chains of the brush entering the core with no penetration giving a value of 1. To account for the rigid CP nanotube at the interface it was set to 1.1.

^f To account for the soft interface between the pure polymer blocks PBA and PPEGA a value for d of 0.8 gave the best results.

Form factor for a micelle with a spherical core

From equation 7, a spherical core was described adapting F_{s(q)}, S_{SC(q)} and S_{CC(q)}:

$$F_{s(q)} = \Phi^2(qR) \text{ with } \Phi(qR) = \frac{3[\sin(qR) - qR \cdot \cos(qR)]}{(qR)^3}$$

$$S_{sc(q)} = \Phi(qR)\psi(qR_g)\frac{\sin(q[R + dR_g])}{q[R + dR_g]}$$

$$S_{cc(q)} = \psi(qR_g)^2\left[\frac{\sin(q[R + dR_g])}{q[R + dR_g]}\right]^2$$

The scattering length densities were calculated according to the respective chemical structure.

The fit (Figure S4) was performed with R, R_g, N_{agg} and N as adjustable parameter. The values afforded by the fit are gathered in Table S2 in the following.

Table S2. Fitting parameters for PBA₂₇-*b*-PPEGA₄₅ using a form factor of a micelle with a spherical core

parameter	values	
N _{agg}	23.0	
R _{core} ^a (Å)	31.5	Fitted
R _{g, corona} ^b (Å)	41.3	
N	7.52 × 10 ⁻²	
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V _{core} ^c (Å ³)	5677.1	
V _{corona} ^c (Å ³)	33160.9	
ρ _{core} ^d (cm ⁻¹)	6.76 × 10 ⁻⁷	Calculated
ρ _{corona} ^d (cm ⁻¹)	7.25 × 10 ⁻⁷	
ρ _{solvent} ^d (cm ⁻¹)	6.39 × 10 ⁻⁶	
d ^e	0.8	
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Background subtracted	1.5 × 10 ⁻³	

^a The radius of the core was calculated from the volume of the whole core given by the volume of the core of a single unit multiplied with the number of aggregation (N_{agg});

^b Radius of gyration (R_g) of a single chain in the corona;

^c The Volume of a single polymer chain in the core (PBA) or corona (PPEGA) was estimated from the M_n, divided by the Avogadro constant and assuming a density of 1.1 g/cm³;

^d The scattering lengths density (SLD) of the materials was calculated using the calculator given in SASfit;

^e d represents a penetration factor for chains of the brush entering the core with no penetration giving a value of 1. To account for the soft interface between the pure polymer blocks PBA and PPEGA a value of 0.8 gave the best results.

5. SANS of PBA₂₃-CP-PPEGA₄₅ in different solvents

- Fit for PBA₂₃-CP-PPEGA₄₅ in DMSO

The first attempt to fit the scattering data of PBA₂₃-CP-PPEGA₄₅ was tried using a form factor for a micelle with a wormlike core (Figure S9). The focus was set on fitting the low q range (0.04 - 0.02 \AA^{-1}) which is indicative for a larger structure, while at higher values of q ($> 0.02 \text{ \AA}^{-1}$) the profile of a Gaussian chain (data proportional to q^{-2}) is observed. The fitting parameters are summarized in the following table (Table S3).

Table S3. Fitting parameters for PBA₂₃-CP-PPEGA₄₅ in deuterated DMSO using a form factor for a wormlike micelle.

parameter	values	
R_{core} (Å)	19.9	
L_{core} (Å)	2442.9	
L_{Kuhn}^a (Å)	458.3	
$R_{g, \text{corona}}^b$ (Å)	56.6	Fitted
N_{agg}^c	1423	
N	4.32×10^{-3}	
<hr/>		
V_{core}^d (Å ³)	7223.13	
V_{corona}^d (Å ³)	33160.9	
ρ_{core}^e (cm ⁻¹)	8.84×10^{-7}	Calculated
ρ_{corona}^e (cm ⁻¹)	7.25×10^{-7}	
ρ_{solvent}^e (cm ⁻¹)	5.28×10^{-6}	
<hr/>		
Background subtracted	3.4×10^{-3}	

^a The Kuhn length of a segment of the wormlike micelle;

^b Radius of gyration (R_g) of a single chain in the corona;

^c The number of aggregation (N_{agg}) was calculated from the volume of the whole core divided by the volume of the core of a single unit;

^d The Volume of a single polymer chain in the core (PBA) or corona (PPEGA) was estimated from the M_n , divided by the Avogadro constant and assuming a density of 1.1 g/cm^3 ;

^e The scattering lengths density (SLD) of the materials was calculated using the calculator given in SASfit.

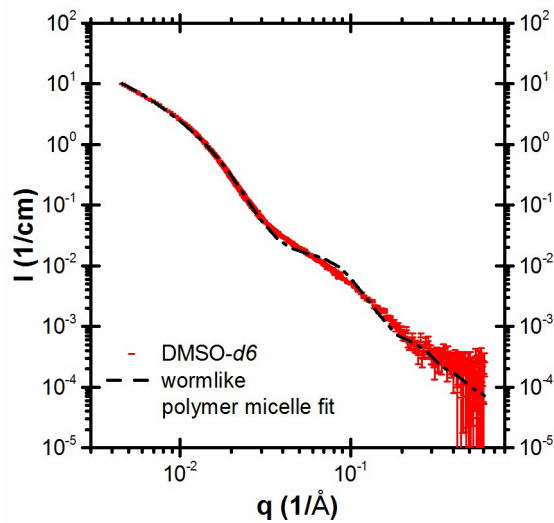


Figure S9. Scattering data (SANS) of PBA₂₃-CP-PPEGA₄₅ in deuterated DMSO (red). The dashed line represents a cylindrical polymer micelle fit.

Although the data was nicely fitted at low q -values, the present wormlike micelle fit could not be well matched with the linear decay at high values of q ($> 0.02 \text{ \AA}^{-1}$). The observed slope at high q is proportional to q^{-2} which is indicative of a Gaussian chain. Therefore, we assume that the scattering data is a superposition of two different scattering profiles, a wormlike micelle and a Gaussian chain.

From scattering experiments on a 1 mg/mL solution in deuterated DMF we observed the typical scattering behavior of a free polymer chain (Gaussian chain, see Figure 4 in the main manuscript). The resulting fitting parameters are summarized in the following table (Table S4).

Table S4. Fitting parameters for PBA₂₃-CP-PPEGA₄₅ in deuterated DMF using a form factor for Gaussian chain.

parameter	values	
$R_{g, \text{conjugate}}^a$ (Å)	72.7	Fitted
N	4.38×10^0	
b_{polymer}^b (Å)	3.04×10^{-3}	Calculated
V_{polymer}^c (Å ³)	40384.0	
ρ_{solvent}^d (cm ⁻¹)	6.33×10^{-6}	
Background subtracted	0	

^a Radius of gyration (R_g) of the conjugate;

^b The scattering lengths b of the polymer was calculated using the calculator given in SASfit;

^c The Volume of the whole conjugate was calculated as the sum of the individual parts;

^e The scattering lengths density (SLD) of the materials was calculated using the calculator given in SASfit.

Comparing the scattering data of the conjugate PBA₂₃-CP-PPEGA₄₅ in DMF and DMSO a similar slope is observed for high q -values ($> 0.02 \text{ \AA}^{-1}$) which is proportional to q^{-2} . Based on these results we tried to fit the scattering data in DMSO by a combination of a form factor for a wormlike micelle and a Gaussian chain. In order to minimize the number of fitting parameters the previously observed values for the fits of the Gaussian chain in DMF were used as fixed parameters and only the radius of the core (R_{core}), the radius of gyration of the corona chains ($R_{g, \text{corona}}$), and the respective parameters N were fitted. The results of the fit (given in Figure 4 in the main manuscript) are summarized in Table S5.

Table S5. Fitting parameters for PBA₂₃-CP-PPEGA₄₅ in deuterated DMSO using a form factor for a wormlike micelle and a Gaussian chain.

parameter	values	
R_{core} (Å)	37.4	
$R_{\text{g, corona}}^a$ (Å)	48.5	Fitted
$N_{\text{wormlike micelle}}$	3.44×10^{-4}	
$N_{\text{Gaussian chain}}$	2.34×10^0	
L_{core} (Å)	2442.9	Fixed (wormlike micelle)
L_{Kuhn}^b (Å)	458.3	
N_{agg}^c	1489	
$R_{\text{g, conjugate}}^d$ (Å)	72.7	Fixed (Gaussian chain)
V_{core}^e (Å ³)	7223.13	
V_{corona}^e (Å ³)	33160.9	
ρ_{core}^f (cm ⁻¹)	8.84×10^{-7}	Calculated
ρ_{corona}^f (cm ⁻¹)	7.25×10^{-7}	
ρ_{solvent}^f (cm ⁻¹)	5.28×10^{-6}	
b_{polymer}^g (Å)	3.04×10^{-3}	
V_{polymer}^h (Å ³)	40384.0	
Background subtracted	3.4×10^{-3}	

^a Radius of gyration (R_{g}) of a single chain in the corona;

^b The Kuhn length of a segment of the wormlike micelle;

^c The number of aggregation (N_{agg}) was calculated from the volume of the whole core divided by the volume of the core of a single unit;

^d Radius of gyration (R_{g}) of the conjugate;

^e The Volume of a single polymer chain in the core (PBA) or corona (PPEGA) was estimated from the M_n , divided by the Avogadro constant and assuming a density of 1.1 g/cm³;

^f The scattering lengths density (SLD) of the materials was calculated using the calculator given in SASfit;

^g The scattering lengths b of the polymer was calculated using the calculator given in SASfit;

^h The Volume of the whole conjugate was calculated as the sum of the individual parts.

As the same concentration (1 mg/mL) was used in both cases, the solution in DMF and in DMSO, the concentration factor $N_{\text{Gaussian coil}}$ of the combined fit could be compared to the value of the initial fit in DMF giving a ratio of not aggregated chains in the solution.

- *PBA₂₃-CP-PPEGA₄₅ in deuterated Acetonitrile, DMF and THF*

The conjugate PBA₂₃-CP-PPEGA₄₅ showed good solubility in a few solvents. However the neutron scattering experiments revealed that in most cases aggregates are still present (Figure S10).

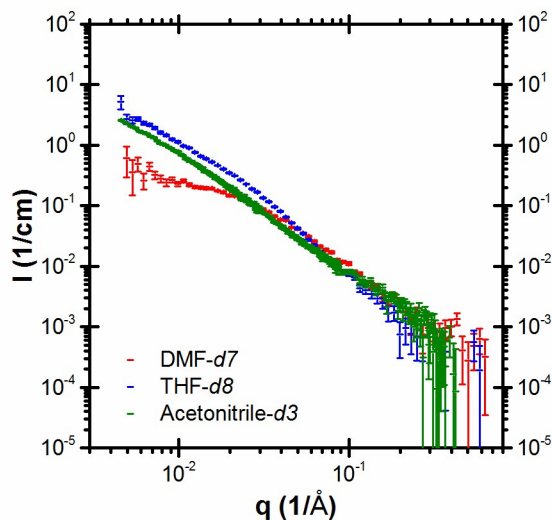


Figure S10. Scattering data (SANS) of PBA₂₃-CP-PPEGA₄₅ in deuterated Acetonitrile, THF, and DMF.

- *PBA₂₃-CP-PPEGA₄₅ in deuterated DMSO and DMF fitted by a Guinier-Porod Model*

SANS data can also be analyzed using standard linear plots such as Guinier or Porod. These plots have the advantage to give estimates of particles size (radius of gyration) and clues as to the nature of the scattering inhomogeneities through the Porod exponent without doing any hypothesis of the shape of the objects. The Porod exponent is of particular interest as it can denote for the quality of the solvent for the individual polymers, as a value of $d = 3$ can point to scattering from collapsed polymer chains (in a bad solvent) whereas a “fully swollen” chain would give a value of $d = 5/3$.

Hammouda has developed a Guinier-Porod-Model adapted to fit shapes as diverse as dissolved polymer chains, spherical micelles, cylindrical micelles or lamellar micelles.⁸ In order to generalize the Guinier-Porod-Model to account for nonspherical scattering objects, the following functional forms are used:

$$I_{(q)} = \frac{G}{q^s} \exp\left(\frac{-q^2 R_g^2}{3-s}\right) \text{ for } q \leq q_1 \quad (\text{equation 8})$$

$$I_{(q)} = \frac{D}{q^d} \text{ for } q \geq q_1 \quad (\text{equation 9})$$

Applying the same continuity of the Guinier and Porod functions and their derivatives yields:

$$q_1 = \frac{1}{R_{g1}} \left[\frac{(d-s_1)(3-s_1)}{2} \right]^{1/2} \quad (\text{equation 10})$$

$$D_1 = G_1 \exp\left(\frac{-q_1^2 R_{g1}^2}{3-s_1}\right) q_1^{(d_1-s_1)} \quad (\text{equation 11})$$

The fit of the SANS data of PBA₂₃-CP-PPEGA₄₅ in DMF has been realized using a simple Guinier-Porod-Model whereas in DMSO a combination of two Guinier-Porod-Models was

necessary to account for the presence of both aggregates and unimers. The resulting fits to the data are shown in Figure S5 and the results are summarized in Table S6.

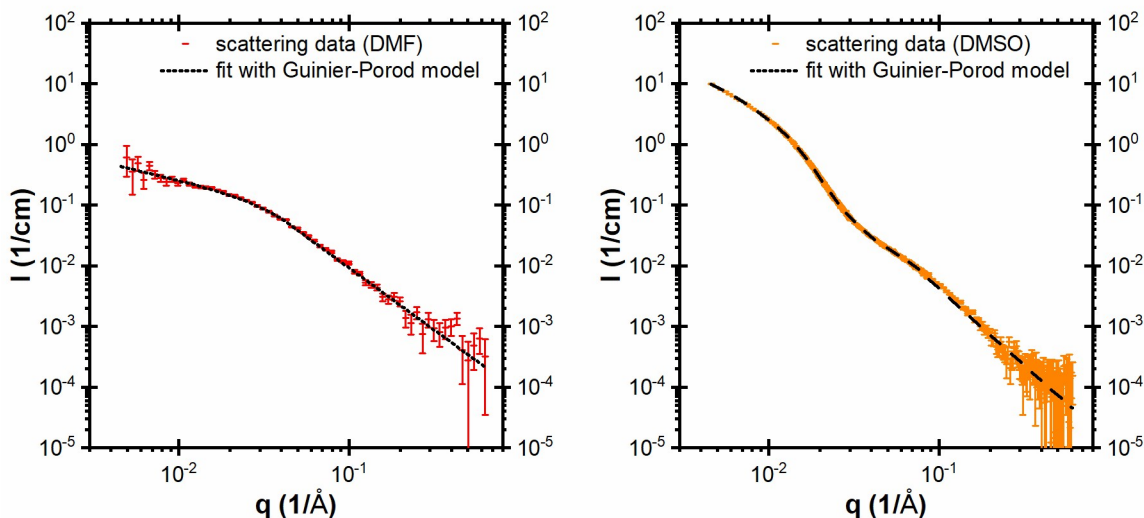


Figure S11. Scattering data (SANS) of PBA₂₃-CP-PPEGA₄₅ in deuterated DMF (left) and DMSO (right) including the respective fits using the above described Guinier-Porod-Model (the data for DMSO was additionally corrected for background scattering).

Table S6. Fitting parameters for PBA₂₃-CP-PPEGA₄₅ in deuterated DMSO and DMF using a Guinier-Porod-Model.

		PBA ₂₃ -CP-PPEGA ₄₅ in deuterated DMF	PBA ₂₃ -CP-PPEGA ₄₅ in deuterated DMSO
Guinier 1	R _{g1} (Å)	29.3	90.6
	G ₁	1.34 × 10 ⁻²	1.13 × 10 ⁻²
	S ₁	0.6	1.28
	Q ₁ (Å ⁻¹)	4.38 × 10 ⁻²	1.80 × 10 ⁻²
Porod 1	d ₁	2.05	4.38
	D ₁	8.31 × 10 ⁻⁵	9.38 × 10 ⁻⁹
Guinier 2	R _{g2} (Å)		24.5
	G ₂		1.88 × 10 ⁻²
	S ₂		5.67 × 10 ⁻²

	Q_2 (\AA^{-1})	8.5×10^{-2}
Porod 2	d_2	2.49
	D_2	1.29×10^{-5}

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