Supplementary Material

S1. Determination of the volume fractions of the small micelles and large aggregates

In the dynamic light scattering experiment (performed on the PDMS-PEO block copolymer system) the scattered field autocorrelation function $g_1(q,t)$ of the diffusing particles (namely the small micelles and the large aggregates) can be expressed as the sum of the two distinct exponential contribution expressed in terms of the decay rate of the diffusing small micelles (Γ_1) and the large aggregates (Γ_2) and in terms of the amplitudes A_1 (for small micelles) and A_2 (for large aggregates) [25]

$$g^{(1)}(t) = A_1 exp(-\Gamma_1 t) + A_1 exp(-\Gamma_2 t) \quad \textbf{(S1)}$$

In order to obtain an estimate of the volume fraction of small micelles φ_1, and of large clusters φ_2, we can use the expressions of the amplitudes A_1 and A_2 of the scattered field autocorrelation function $g_1(q,t)$:

$$\frac{A_2}{A_1} = \frac{C_2 I_2(M_{W2},\theta)}{C_1 I_1(M_{W1},\theta)} \quad \textbf{(S2)}$$

where C_i is the concentration of each scatterer in mg ml^{-1}, $I_i(M_i,\theta)$ is the intensity scattered at angle θ by scatterer i per unit concentration of i; M_i is the molecular weight of scatterer i. The concentration C_i is related to number density n_i as $C_i=(M_i \cdot n_i)/N_A$, where N_A is Avogadro's number. The intensity I_1 of light scattered by a generic aggregate can be obtained from the expression for the Rayleigh ratio $R(q)$ of the scattered (I_1) to incident (I_0) intensity for small interacting molecules

$$R(q) = K M_w c P(q) S(q) \quad \textbf{(S3)}$$

where the optical constant K [25], while $P(q)$ and $S(q)$ are the normalized form factor and the structure factor respectively, M_w the molecular weight, c the mass concentration (in g/ml). The previous equation can be expressed in the following form

$$\frac{Kc}{R(q)} = \frac{1}{M_w} \cdot \frac{1}{P(q)} \cdot \frac{1}{S(q)} \quad \textbf{(S4)}$$

Considering that two different typology of scattering aggregates (i.e. micelles and large aggregates) are present in solution, we can calculate the previous expression for the two typology of scattering object in the system.

For the small micellar aggregates the previous equation can written as [25]:

$$\frac{K_1 C_1}{R_1(q)} = \frac{1}{M_{w1}} \cdot f(C_1)$$

(S5)

where $f(C_1) \approx 1 + M_1(2B_2C_1$ and B2 is the second virial coefficient,)and assuming that for the small micelles the form factor $P_1(q)$ is equal to 1.

For the larger aggregates (assuming $S(q) \approx 1$ for low clusters concentration) we have the following relation:

$$\frac{K_2 C_2}{R_2(q)} = \frac{1}{M_{w2} P(qR_2)}$$

(S6)

Where $P(qR_2) = [3J_1(qR_2)/(qR_2)]^2$ is the form factor of the large aggregates with radius R_2, where $J_1(x) = [sin(x) - x \cdot cos(x)]/x^2$ is the first-order spherical Bessel function [27].

Taking into account the last two equations (5) and (6), the Equation (2) can be written as:

$$\frac{A_2}{A_1} = \frac{C_2 K_2 M_{W2}}{C_1 K_1 M_{W1}} P(qR_2) f(C_2)$$

(S7)

Assuming the same refractive index increments $\partial n_i / \partial C_i$ and the same density (i.e. $\rho_1 = \rho_2$) for two different population of scattering aggregates and defining the volume fraction of clusters as $\varphi_i = n_i(4/3 \cdot \pi R_i^3)$, and molecular weight $M_{wi} = \rho_i(4/3 \cdot \pi R_i^3)$, we finally get

$$\frac{\varphi_2}{\varphi_1} = \frac{A_2}{A_1} \cdot \frac{1}{P(qR_2)} \cdot \frac{1}{[1 + 2B_2 C_1]} \cdot \left(\frac{R_1}{R_2}\right)^3$$

(S8)

This expression has been used to estimate the volume fraction φ_1 (for micelles) and φ_2 (for large aggregates) detected in the water/PDMS-PEO block copolymer system, as reported in the **Fig, 9** of the article.

S2. Determination of the PDMS-PEO c.m.c. in the temperature range 10≤T≤55 °C

In this section, we report the determination of the critical micellar concentration (c.m.c.) for the water solution of the PDMS-PEO block copolymer system in the temperature range 10≤T≤55 °C by measuring the absolute excess scattered intensity, R as a function of block copolymers concentration, in c(g/cm^3).

The plot of the absolute intensity $Kc/R90°$ at the scattering angle of θ=90° as a function of the PDMS-PEO block copolymer concentration identifies (with its minimum) the critical micelles concentration (c.m.c) for each of the 5 investigated temperatures investigated (namely T=10, 15, 25, 35, 45, 55 °C), as reported in the insert of Figure S1. The plot evidences a weak dependence with temperature of the detected c.m.c.
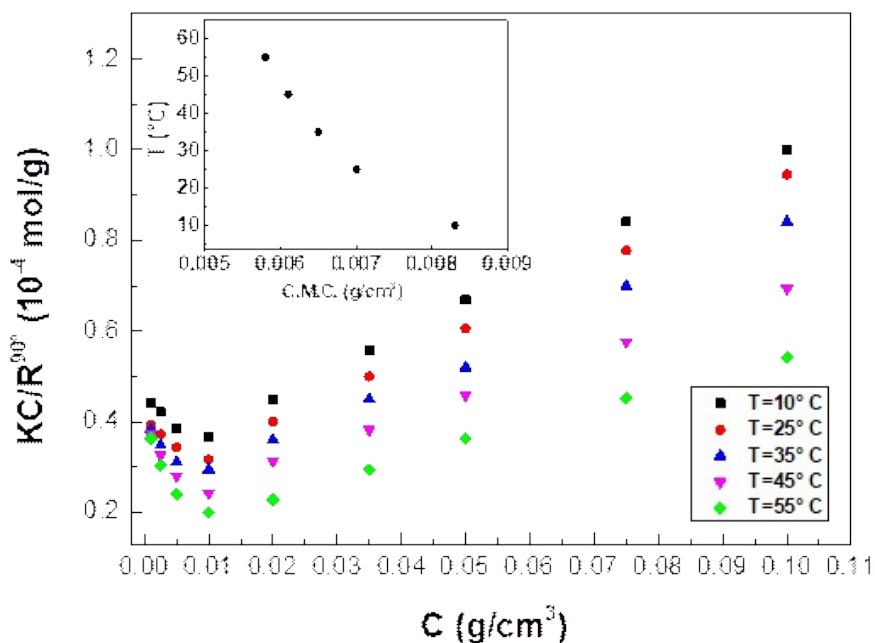

Figure S1. Normalized inverse excess scattered intensity Kc/R90° as a function of the PDMS-PEO block copolymer concentration C(g/cm^3), for 5 different temperatures in the range 10≤ T≤55 °C.