Supplementary Information

Self-assembly in casting solutions of block copolymer membranes

Small angle x-ray scattering data

Table S1. Values of q/q* for PS-b-P4VP 175k-*b*-65k solutions in 1:1:1 DMF:THF:DOX; *d*-spacing for the first peak; full width at half maximum (FWHM)

PS-*b*-P4VP 175k-*b*-65k 1:1:1 DMF:THF:DOX							
Polymer Conc. (wt%)	q/q*				Structure	d-spacing (nm)	FWHM (10^{-3}/nm)
16	1	1.74	2.04		2D hexagonal	74	8
17	1	1.73	1.97	2.63	2D hexagonal	76	8
19	1	1.74	1.92	2.67	2D hexagonal	75	7
22	1	1.73	2.63	2.97	2D hexagonal *	80	10
24	1	1.77	2.76		2D hexagonal *	86	33

missing peak at q/q*=2

Table S2. Values of q/q* for PS-b-P4VP 330k-*b*-125k solutions in 1:1:1 DMF:THF:DOX; *d*-spacing for the first peak

PS-*b*-P4VP 330k-*b*-125k 1:1:1 DMF:THF:DOX					
Polymer Conc. (wt%)	q/q*			Structure	d-spacing (nm)
16	1	1.89	2.61	Non-identified	105
22	1	2.50	3.72	Non-identified	99

Table S3. Values of q/q* for PS-b-P4VP 175k-*b*-65k solutions in binary solvents; *d*-spacing for the first peak; full width at half maximum (FWHM)

PS-*b*-P4VP 175k-*b*-65k 1:1 DMF:THF							
Polymer Conc. (wt%)	q/q*				Structure	d-spacing (nm)	FWHM (10^{-3}/nm)
18	1				disordered	71	28
20	1	1.74			2D hexagonal	72	11
22	1	1.73	2.64	2.98	2D hexagonal*	74	11
24	1	1.70	2.62	2.93	2D hexagonal *	82	12

missing peak at q/q*=2

PS-*b*-P4VP 175k-*b*-65k in 1:1 DMF:DOX								
Polymer Conc. (wt%)	q/q*					Structure	d-spacing (nm)	FWHM (10^{-3}/nm)
14	1					disordered	73	63
16	1	1.75				2D hexagonal*	73	35
17	1	1.74				2D hexagonal*	73	31
18	1	1.75				2D hexagonal*	74	28
19	1	1.74	2.64	2.99		2D hexagonal *	75	22
20	1	1.73	2.63	3.04	3.58	2D hexagonal *	74.	11
21	1	1.73	2.65	2.97		2D hexagonal *	80	10
22	1	1.74	2.64			2D hexagonal *	77	11
24	1	1.73	2.63			2D hexagonal *	77	10

missing peak at q/q*=2

PS-*b*-P4VP 175k-*b*-65k in 1:1 THF:DOX							
Polymer Conc. (wt%)	q/q*				Structure	d-spacing (nm)	FWHM (10^{-3}/nm)
18	1	1.60	2.85	4.57	Non-identified	94	25
20	1	1.60	2.70	4.34		89	26
22	1	1.62	2.77	4.45		91	22
24	1	1.60	2.54	4.09		87	24

Table S4. Values of *q*/*q** for PS-*b*-P4VP 175k-*b*-65k solutions; d-spacing for the first peak and full width at half maximum (FWHM)

PS-*b*-P4VP 175k-*b*-65k									
Polymer Conc. (wt%)	DMF:THF:DOX Solvent ratio	q/q*					Structure	d-spacing (nm)	FWHM (10^{-3}/nm)
15	1:1:1	1					2D hexagonal*	74	13
21	1:0:1	1	1.73	2.65	2.97		2D hexagonal*	80	10
23	5:0:4	1	1.73	2.62			2D hexagonal*	77	11
26	2:0:1	1	2.03	3.04	4.06	5.11	Lamellar	83	15
35	1:0:0	1	1.99	2.99	3.97		Lamellar	89	12

missing peak at q/q*=2

Table S5. Values of *q*/*q** for PS-*b*-P4VP 175k-*b*-65k solutions with 0.15 wt % copper acetate; *d*-spacing for the first peak and full width at half maximum (FWHM)

PS-*b*-P4VP 175k-*b*-65k in solutions with 0.15 wt % Cu^{2+}									
Polymer Conc. (wt%)	DMF:THF:DOX Solvent ratio	q/q*					Structure	d-spacing (nm)	FWHM (10^{-3}/nm)
5	7:3:0	1	1.58				Disordered	86	28
15	7:3:0	1	1.62				Disordered	68	33
18	7:3:0	1	1.72	1.96			2D Hexagonal	71	14
19	7:3:0	1	1.72	1.83	2.60		2D Hexagonal	72	19
20	7:3:0	1	1.72	1.93	2.62	2.95	2D Hexagonal	73	15
22	7:3:0	1	1.95	1.72	2.62	2.97	2D Hexagonal	73	15
26	1:0:0	1	2.02	3.02	4.05	4.71	Lamellar	76	13

Table S6. Values of *q*/*q** for 20 wt % PS-*b*-P4VP 175k-*b*-65k solutions in 7:3 DMF:THF with 0.15 wt % of metal acetates; *d*-spacing for the first peak and full width at half maximum (FWHM)

PS-*b*-P4VP 175k-*b*-65k in solutions with 0.15 wt % Metal salt								
Metal ion	q/q*					Structure	d-spacing (nm)	FWHM (10^{-3}/nm)
no	1	1.78				Disordered	74	27
Cu2+	1	1.72	1.93	2.62	2.95	2D Hexagonal	73	15
Ni2+	1	1.84				2D Hexagonal	78	17
Co2+	1	1.25	2.53	3.78		2D Hexagonal*	75	13
Fe2+	1	1.77	1.87	2.12	2.56	2D Hexagonal	75	10

missing peak at q/q*=2

Dissipative Particle Dynamics – DPD

DPD is a stochastic particle model introduced by Hoogerbrogge and Koelman [1], later updated by Espanol and Warren [2] updated the DPD method, stating it statistical mechanics framework. One of the most important implementation of DPD is the study of polymers, colloids, amphiphiles, and mixtures. Many applications have been reported in the last 10 years, some include microphase separation in diblock copolymers, spinodal decomposition in binary immiscible fluids.
The DPD model consists in the interaction of a group of soft spheres (beads or particles) that are described by a single point, with position $\mathbf{r_i}$, and soft repulsive interaction up to a certain cutoff radius r_c. The velocity and the net force acting over each particle can be defined respectively as: $v_i = dr_i = dt$ and $f_i = m_i\, dv_i = dt$; where m_i is the mass of the particle.
The applied force to each particle, has three different contributions:

$$f_i = \sum_{j \neq i} (F_{ij}^C + F_{ij}^D + F_{ij}^R) \qquad (1)$$

where F_{ij}^C is a conservative force, that mimics the pressure effects between particles. Usually this force is represented by a repulsive soft potential. F_{ij}^D mimics the dissipative (viscous) interaction in a fluid and can be viewed as a friction force that reduces the velocity differences between particles. F_{ij}^R is a stochastic force (random) that takes into account the random collisions between particles, and from the molecular dynamics point of view includes the degrees of freedom lost during the coarse-graining process. This stochastic force will reproduce the Brownian motion of polymers and colloids for example.
The conservative force term has the form:

$$F_{ij}^C = \left\{ \begin{matrix} a_{ij}\omega^C \hat{e}_{ij};(r_{ij} < r_C), \\ 0;(r_{ij} \geq r_C) \end{matrix} \right\} \qquad (2)$$

where a_{ij} is the maximum repulsion between particles i and j , is a weighting function that gives the range of interaction between particles; r_c is the cutoff radius, $r_{ij} = r_i - r_j$,
$r_{ij} = \left| r_{ij} \right|, \hat{e}_{ij} = r_{ij} / \left| r_{ij} \right|$

The remaining forces are defined as:

$$F_{ij}^D = -\gamma\omega^D(r_{ij})(\hat{e}_{ij}.v_{ij})\hat{e}_{ij} \qquad (3)$$
$$F_{ij}^R = \sigma\omega^R(r_{ij})\zeta\Delta t^{-1/2}\hat{e}_{ij} \qquad (4)$$

where γ is a friction coefficient that determines the overall magnitude of the dissipative term, and σ is a noise amplitude that scales the stochastic contribution. ω^D and ω^R are weight functions that vanish for $r > r_c$, for each pair of particles; ζ is a random number with zero mean and unit variance. From the fluctuation - dissipation theorem, and in order to satisfy a Gaussian distribution, the next relationship between the dissipative and the random force must be satisfied:

$$\omega^D(r) = \left[\omega^R(r)\right]^2 \tag{5}$$

$$\sigma^2 = 2\gamma k_B T \tag{6}$$

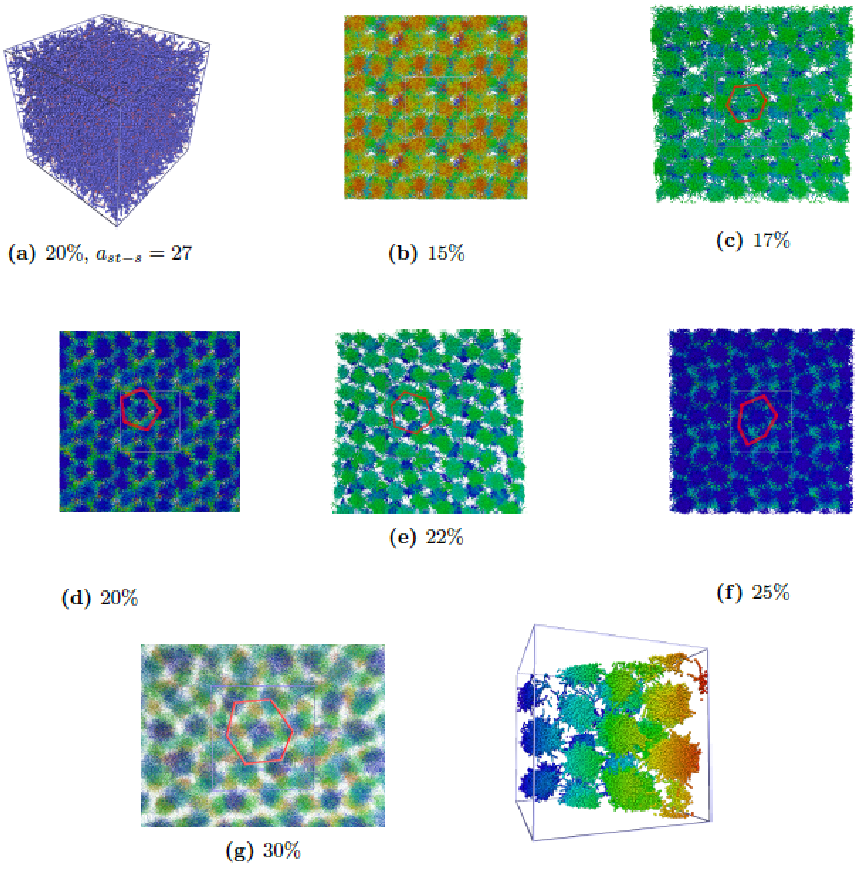
where k_B is the Boltzmann constant and T is the equilibrium temperature. Due to its simplicity, the following definition for the weighting random function is commonly used in the literature (eq. 7), where $\omega^R(r)$ is assumed to vary linearly away from the particle, as the conservative force does, leading:

$$\omega^D(r) = \left[\omega^R(r)\right]^2 = \begin{Bmatrix} (1 - r/r_e)^2; (r < r_e), \\ 0; (r \geq r_e) \end{Bmatrix} \tag{7}$$

Simulation details

All the simulations were carried out in the software LAMMPS [3] with the common choices for the length, mass and time units in DPD [4]. For simplicity, the length unit is related with the cutoff radius $1r_c$; for the mass units, the simplification assumes that all the beads have the same mass, and $m_i = 1$. The time unit (**τ**) is fixed by choosing the energy units as $1k_BT$, the selected time for the simulations in this paper was 0.05 **τ** . This time scale on DPD it has been usually associated with process on the order of nano and micro-seconds, depending the specific coarse-graining procedure used. The simulation box size for the systems treated was $(50\mathbf{r_c})^3$ (approximately $(180\text{nm})^3$), with a particle density $\rho = 3$ particle $= (r_c)^3$. The total time steps for all the runs were fixed on 500000 $\Delta\boldsymbol{\tau}$, including a stabilization period of 20.000 time steps. During the stabilization stage, all the interaction parameters had the same value $a_{ij} = 25$. The interaction parameters styrene-solvent, a_{st-s} were systematically varied from 25 to 60, simulating the transition from weakly to highly bad solvents, for the PS core. In addition, the evaluated range of polymer concentration corresponds to the experimental data of this paper, from 10% to 30%.

In the Figure S1, the characteristic self-assembled structures can be seen as the concentration of polymer increases in a weakly bad solvent. In this case it has been associated with $a_{st-s} = 30$, and it can be understood as a representation of the DMF: THF:DOX mixture. In general, based on the experimental evidence and the simulation results, it was possible to match qualitatively a consistent tendency regarding the self-assembling process. As the DMF- THF-DOX mixture has been associated qualitatively to $a_{st-s} = 30$, we assume that mixtures like THF-DOX could be represented by $a_{st-s} < 30$; the Figure 1S with $a_{st-s} = 27$ is included showing no evidence of order, such as in the THF-DOX mixture.



(a) 20%, $a_{st-s} = 27$ **(b)** 15% **(c)** 17%

(d) 20% **(e)** 22% **(f)** 25%

(g) 30% **(h)** 30%. Diagonal cut view

Figure S1: Typical micellar patterns found in simulations with bad solvent for the PS, $a_{st\text{-}s}$ = 30. As the concentration increase, the initially disordered micelles (15%) started to pack closer, passing throw hexagonal multilayers (2D Hex) (~17-22%), up to hexagonal close packing (30%). In the concentration of 30% a hexagonal multilayer arrangement can be observed (g). A diagonal section of the system at 30% is included to show it close packing configuration. Gradient of color is applied in the view orientation in order to facilitate the identification of micelles layers. Solvent beads are omitted to make easy the visualization

References

1. P. Hoogerbrugge and J. Koelman, *EPL (Europhysics Letters)*, 1992, **19**, 155.
2. P. Espanol and P. Warren, *EPL (Europhysics Letters)*, 2007, **30**, 191.
3. S. Plimpton, *Journal of Computational Physics*, 1995, **117**, 1-19.
4. R. D. Groot and P. B. Warren, *The Journal of chemical physics*, 1997, **107**, 4423.