

Supporting Information

Synthesis of Highly Porous Poly(*tert*-butyl acrylate)-*b*- polysulfone-*b*-poly(*tert*-butyl acrylate) Asymmetric Membranes

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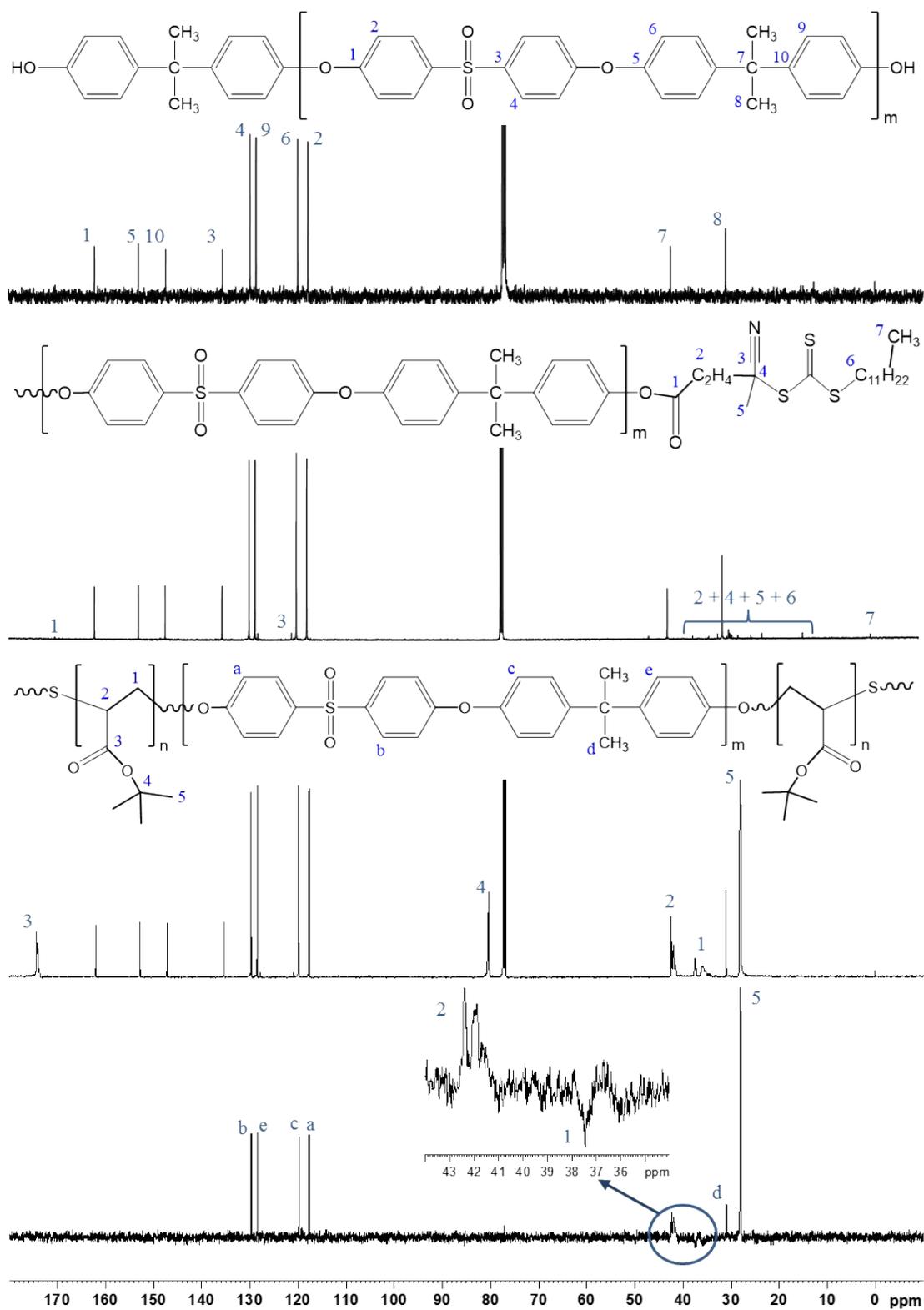


Figure S1. ^{13}C NMR spectra for HO-PSU-OH, CTA-PSU-CTA, PtBA-PSU-PtBA recorded in CDCl_3 . DEPT ^{13}C NMR of PtBA-PSU-PtBA with 135° pulse angle is shown on the bottom. Note the negative peak corresponds to $-\text{CH}_2-$ while primary and tertiary carbons are positive.

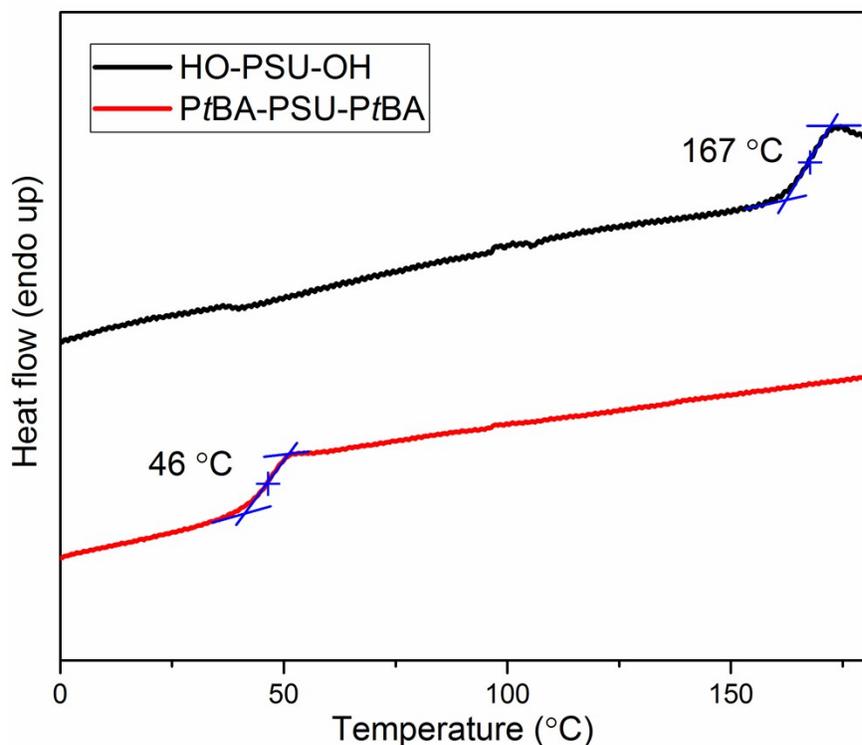


Figure S2. DSC curves for HO-PSU-OH and PtBA-PSU-PtBA. The glass transition temperature (T_g) of HO-PSU-OH is 167 °C, and that of PtBA-PSU-PtBA is 46 °C.

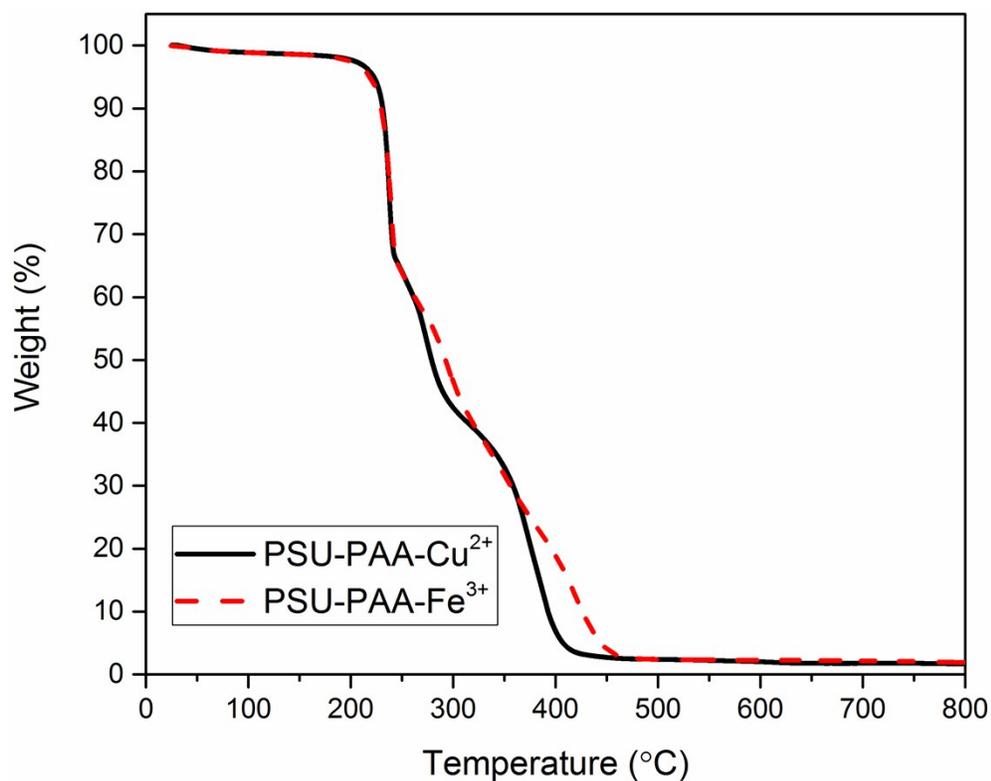


Figure S3. TGA curves for PSU-PAA-Cu²⁺, PSU-PAA-Fe³⁺ under air.

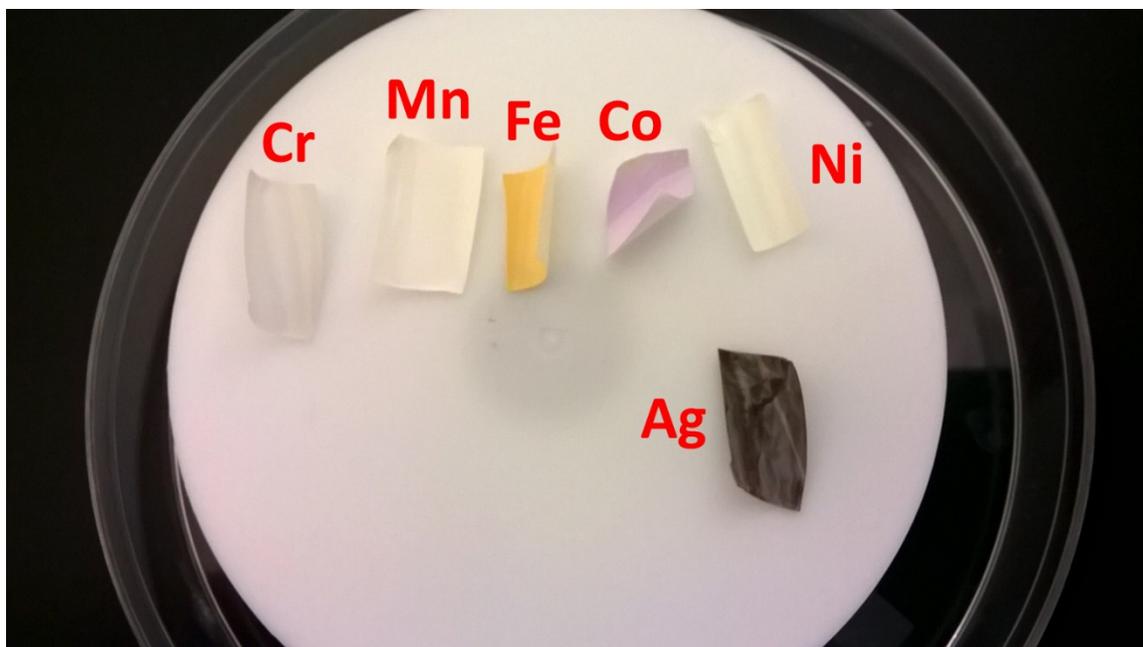


Figure S4. Membranes complexed with various transition metals after acid hydrolysis.

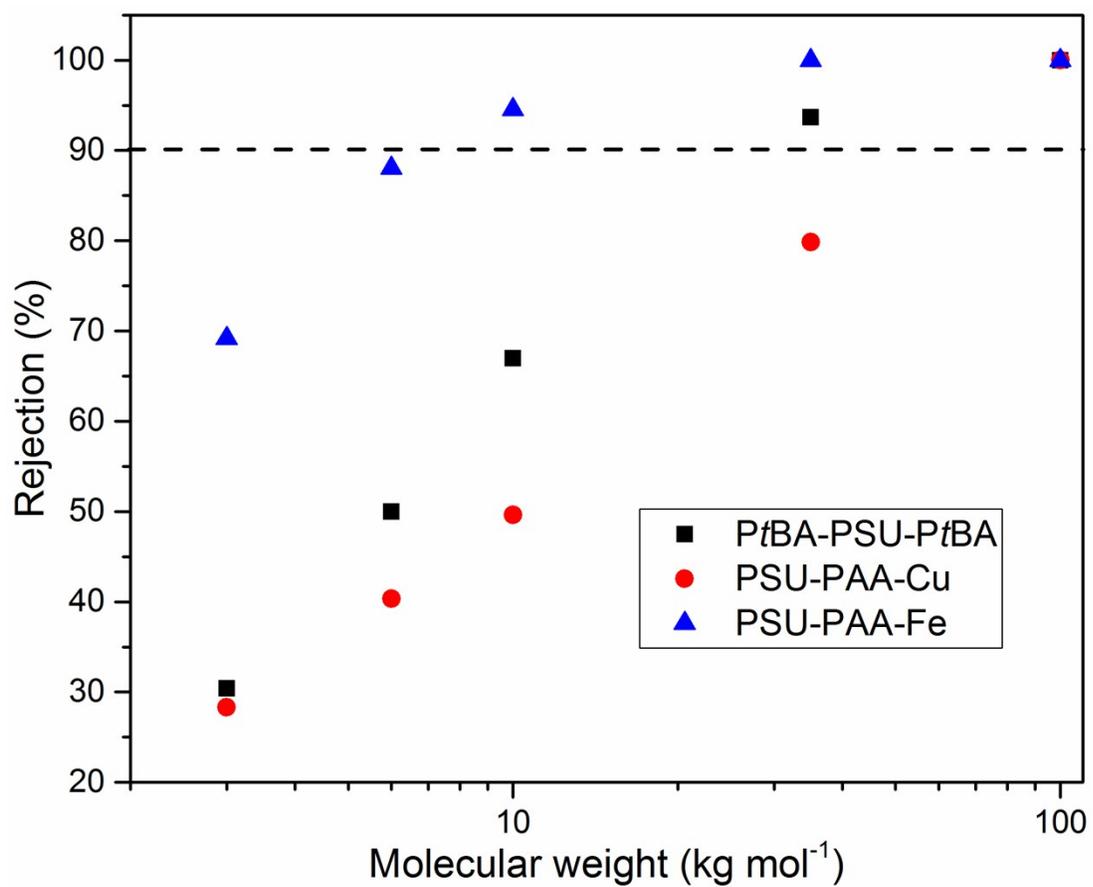


Figure S5. Rejection of poly(ethylene glycol) for the original and modified membranes as a function of molecular weight.

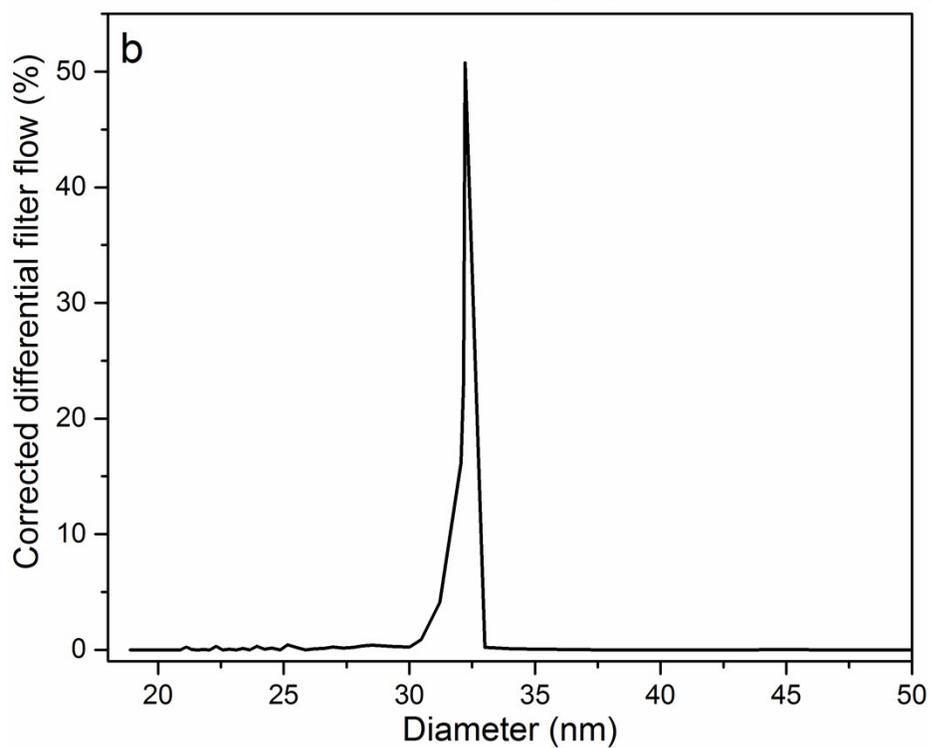
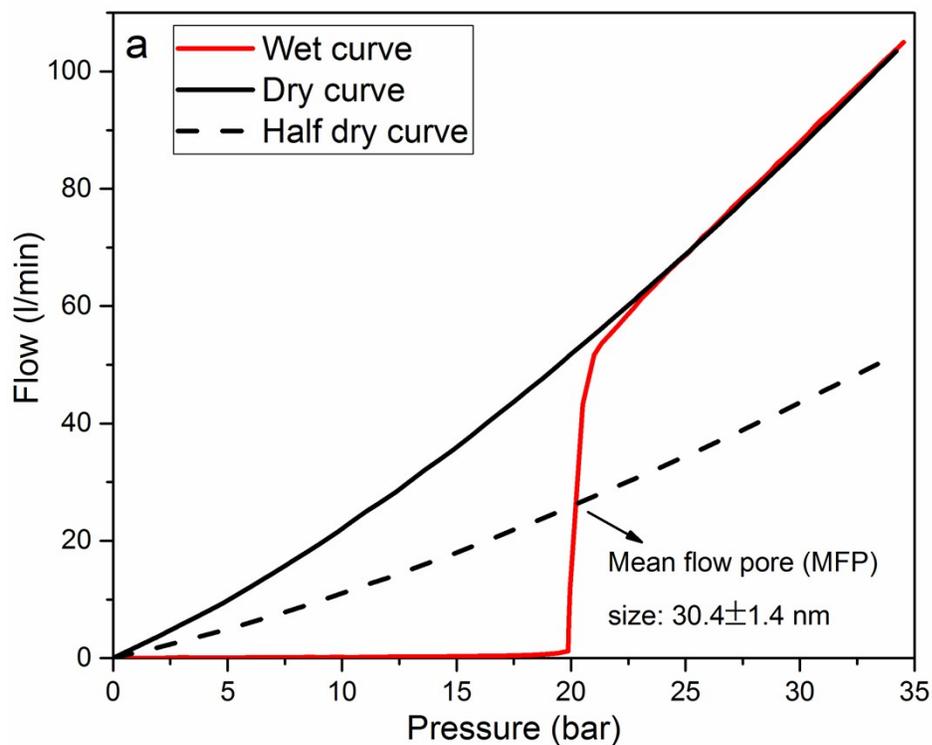


Figure S6. Flow-pressure curve (a) and pore size distribution (b) of PtBA-PSU-PtBA membrane obtained from capillary flow porometry.

Computational Model

Dissipative Particle Dynamics (DPD) Method

In DPD the dynamics and the balance of linear momentum are given by

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i,$$
$$m_i \frac{d\mathbf{v}_i}{dt} = \mathbf{f}_i = \sum_{j \neq i} (\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R),$$

where \mathbf{r}_i , \mathbf{v}_i are the position and velocity of a particle i , respectively, m_i is its mass, and \mathbf{f}_i is the net force on the particle. F_{ij}^C is a conservative contribution that models the affinity between particles, and can be related with the Flory-Huggins interactions parameters.^[1] The term F_{ij}^D is a dissipative contribution that models viscous effects, and F_{ij}^R is a stochastic force. For polymeric systems the conservative force is decomposed in bead-bead (F_{ij}^B) and bead-spring (F_{ij}^S) (when particles are connected) interactions, where $F_{ij}^C = F_{ij}^B + F_{ij}^S$. In this work, the bead-bead and bead-spring potentials are given by

$$u_{ij}^B = \frac{a_{ij}}{2r_c} (r_{ij} - r_c)^2,$$

$$u_{ij}^S = \frac{K_s}{2} (r_{ij} - r_o)^2,$$

where a_{ij} accounts for the affinity between species i and j , K_s is the spring constant, and r_o is the equilibrium distance between connected particles.

The dissipative and random forces are defined as

$$\mathbf{F}_{ij}^D = -\gamma \omega^D(r_{ij}) \left(\frac{\mathbf{r}_{ij}}{|\mathbf{r}_{ij}|} \cdot \mathbf{v}_{ij} \right) \frac{\mathbf{r}_{ij}}{|\mathbf{r}_{ij}|},$$

$$\mathbf{F}_{ij}^R = \sigma \omega^R(r_{ij}) \zeta \Delta t^{-1/2} \frac{\mathbf{r}_{ij}}{|\mathbf{r}_{ij}|},$$

where ω^D and ω^R are weighting function, such that $\omega^D(r_{ij}) = [\omega^R(r_{ij})]^2$, γ and σ are the friction coefficient and the noise amplitude, respectively. The term ζ is a random number with zero mean and unit variance. The parameters γ and σ are related by $\sigma^2 = 2\gamma k_B T$, where k_B is the Boltzmann constant and T is the equilibrium temperature. The most common form of the potential $\omega^D(r_{ij})$ is given by

$$\omega^D(r_{ij}) = [\omega^R(r_{ij})]^2 = \begin{cases} (1 - r_{ij}/r_c)^2; & (r_{ij} < r_c), \\ 0; & (r_{ij} \geq r_c), \end{cases}$$

Simulation Details

Triblock copolymers BAB were constructed using spring potentials, with spring constant $K_s = 50k_b T$ and equilibrium distance $r_o = 0.8$. The PtBA_{30k}-PSU_{14k}-PtBA_{30k} molecules are discretized using 148 particles, while the solvent is modeled as a set of single solvent particles with a polymer-solvent interaction. The size of block is defined from the experimental composition of the block copolymer. The study of the polymer concentration influence over the morphology of the micelles, the amount of BAB in the simulations was varied from 2 to 18%.

According to the Flory-Huggins (F-H) interaction parameters the interaction parameters a_{ij} of the DPD model can be defined.^[1] We choose a_{ij} according to the solvent quality for each block.^[2] The F-H parameters (χ_{is}) can be derived from the solubility parameters of the polymer and solvent (*i.e.*, δ_i and δ_s) by the equation

$$\chi_{is} = \frac{V_s}{RT}(\delta_i - \delta_s)^2,$$

where R , T are the gas constant and temperature, respectively. $V_s = 92.5 \text{ cm}^3/\text{gmol}$ is the molar volume of the solvent, DMAc. The solubility parameters can be computed from the Hansen's solubility parameters^[31] (*i.e.*, dispersive δ_d , polar δ_p , and hydrogen bond δ_h interactions), presented in Table 1. The solvent quality and the phase diagram of the block copolymer solutions are governed by enthalpic (χ) and entropic (N) contributions, where N is the degree of polymerization. This contributions are typically expressed as the product, χN . In Table S2 the computed values of χ and χN are presented. Based on the magnitude of the F-H interactions the solvent is slightly poorer with PtBA block ($\chi > 0.5$), while is practically a theta solvent ($\chi \approx 0.5$) for the PSU block. In the case of PtBA we must note that despite the larger value of the F-H parameter, it is known that the homopolymer is soluble in DMAc. Therefore we use the magnitude of these parameters as a reference of the relative affinity between the species with the solvent.

Herein the affinity between the constituent is given by $\Delta a_{ij} = a_{ij} - a_{ss}$, where $a_{ss} = 25.0$ is the solvent-solvent interactions. Interactions between components of the same type were chosen equal for any specie i (*i. e.*, $a_{ii} = 0$). Supplementary Table S1 compiles the values of Δa used in all the simulations.

Table S1. DPD interaction parameters used in the modeling of BAB block copolymer self-assembly

$\Delta a_{ij} = a_{ij} - a_{ss}$	PtBA	PSU	DMAc
PtBA	0.0	6.0	5.0
PSU		0.0	3.0
DMAc			0.0

Table S2. Flory-Huggins interaction parameters computed for the blocks PtBA_{30k} and PSU_{14k} in DMAc

	$\chi_{polymer-solvent}$	χN
PtBA	1.35	40.
PSU	0.49	7

Reference:

- [1] R. D. Groot, P. B. Warren, The Journal of Chemical Physics 1997, 107, 4423.
- [2] N. Moreno, S. P. Nunes, K.-V. Peinemann, V. M. Calo, Macromolecules 2015, 48, 8036.
- [3] C. M. Hansen, Hansen solubility parameters: a user's handbook, CRC press, 2007.