

## Electronic Supplementary Information for:

# Highly Distensible Nanostructured Elastic Hydrogels from AB Diblock and ABA Triblock Copolymer Melt Blends

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### Contents

- (1) Determination of SOS triblock copolymer concentration in **SOS-72.0** by regression analysis
- (2) Differential scanning calorimetry (DSC) data for the **S-OH** and **SO** samples
- (3) Melt-state rheological analysis of the **SO** and **SOS-72.0** samples
- (4) Additional notes on the analysis of morphology from SAXS

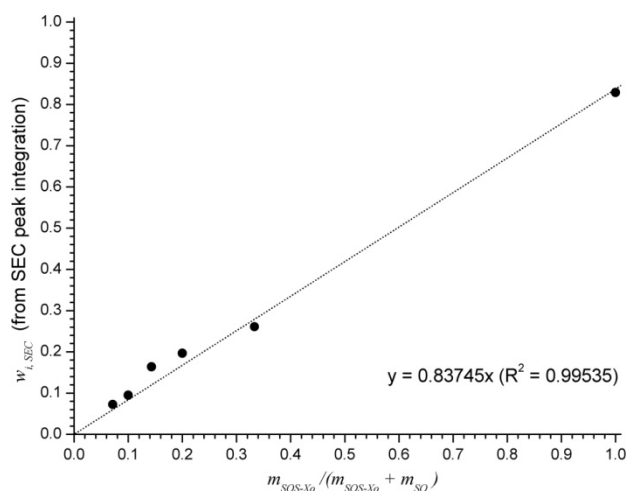
### Data

#### Determination of SOS triblock copolymer concentration in SOS-72.0 by regression analysis

The coupling efficiency of the **SOS-72.0** sample (referred to as SOS- $X_0$  below) was determined using linear least squares regression of the following equation, as described in the primary manuscript:

$$w_{i,SEC} = w_0 \cdot \left( \frac{m_{SOS-X_0}}{m_{SOS-X_0} + m_{SO}} \right) \quad (1)$$

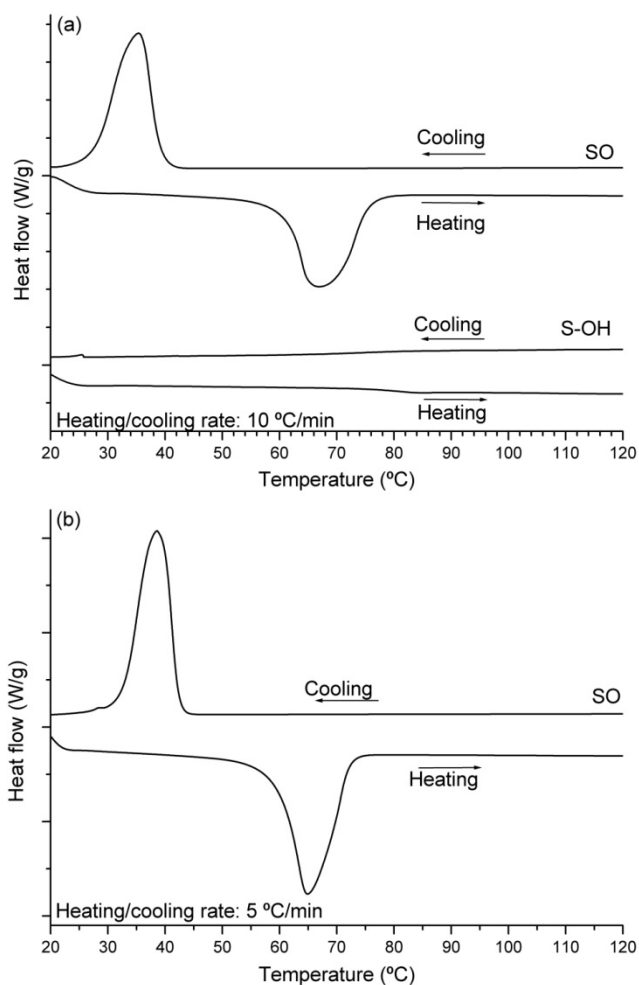
Here,  $w_{i,SEC}$  represents the weight fraction of triblock copolymer in blend sample  $i$ , determined by integrating the relative areas under the SEC chromatogram, and the term in parentheses represents the weight fraction of the **SOS- $X_0$**  sample added to the blend. By plotting the pairs of these values for each blend in Table 2, the mass fraction of triblock copolymer in **SOS- $X_0$** ,  $w_0$ , could be obtained from the slope of the regressed line (Fig. S-1). This analysis gave  $w_0 = 0.837$ , which equates to a molar concentration of triblock copolymer,  $X_0 = 72.0$  mol.



**Fig. S-1** The determination of  $w_0$  by linear regression helps minimize error associated with integrating relative chromatogram peak intensities in cases (such as those found here) where peaks are both partially overlapping and of significantly different intensities. Compare with Fig. 4 in the primary manuscript.

#### Differential scanning calorimetry (DSC) data for the S-OH and SO samples

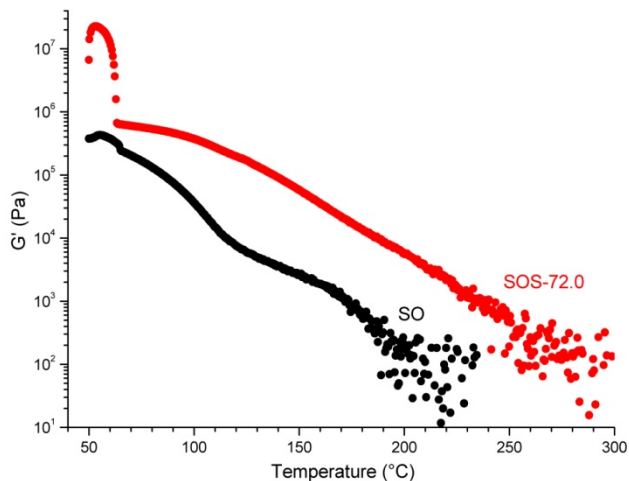
As discussed in the primary manuscript, DSC data was collected for the **S-OH** and **SO** samples using a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ . The **S-OH** bulk PS sample (7.0 mg) exhibited a glass transition at  $80.16 \text{ }^\circ\text{C}$ , however no such transition was detected in the **SO** (6.2 mg) sample (Fig. S-2a). Subsequent data collected on double the amount (12.7 mg) at  $5 \text{ }^\circ\text{C min}^{-1}$  showed no detectable differences (Fig. S-2b).



**Fig. S-2** (a) DSC data for **S-OH** and **SO** samples ( $10 \text{ }^\circ\text{C min}^{-1}$ ). (b) DSC data for **SO** ( $5 \text{ }^\circ\text{C min}^{-1}$ ).

### Melt-state rheological analysis of the SO and SOS-72.0 samples

Melts of both **SO** and **SOS-72.0** samples exhibited elastic moduli in the  $10^3 - 10^5$  Pa range (typical of ordered block copolymer melts) up to 150 °C (Fig. S-3). The transitions detected at around 65 °C correspond to the melting transition of PEO. The lack of a plateau region is typical of spherical morphologies with more liquid-like order.



**Fig. S-3** Dynamic temperature ramp data (oscillatory shear) for the **SO** and **SOS-72.0** samples. Data were collected at  $1\text{ °C min}^{-1}$  at a frequency of  $1\text{ rad s}^{-1}$  and a strain of 2%.

#### Additional notes on the analysis of morphology from SAXS

The determination of the bcc unit cell lattice constant and the PS spherical domain radii from the SAXS data for the **SO** and **SOS-72.0** melts was based on the assumption that the principal scattering wave vector corresponded to the first allowed reflection for the Im3m (bcc) space group. The first allowed reflection corresponds to the 110 family of crystal planes, for which the d-spacing is given by:

$$d_{110} = \frac{2\pi}{q_{110}} \quad (2)$$

This distance corresponds one half of the face diagonal, such that the unit cell lattice constant is given by:

$$a_{bcc} = \sqrt{2}d_{110} \quad (3)$$

If one assumes that all of the PS is located within the spherical domains, then the radii of the PS domains can be estimated since the volume fraction of PS is known. Recalling the bcc lattice contains 2 complete spheres, the volume occupied by a sphere is:

$$V_{PS} = \frac{f_{PS} \cdot (\sqrt{2}d_{110})^3}{2} \quad (4)$$

And its radius is:

$$R_{PS} = \left( \frac{3}{4\pi} \cdot \frac{f_{PS} \cdot (\sqrt{2}d_{110})^3}{2} \right)^{1/3} \quad (5)$$

Finally, once the radius of the sphere is known, the aggregation number can be estimated using the density and molecular weight of the PS block:

$$\theta_{PS} = \left( \frac{4}{3} \pi R_{PS}^3 \right) \left( \frac{\rho_{PS}}{M_{n,PS}} \right) N_A \quad (6)$$

Note that this expression was used to calculate the aggregation numbers of the PS domains for both cases, that is when the radius was estimated using the bcc lattice as an approximation, and when the radius was determined using the more rigorous PY model to fit the SAXS data.

Finally, the nonlinear algebraic function  $G(q, R_{hs}, \phi_{hs})$  used in  $S(q, R_{hs}, \phi_{hs})$  is:

$$\begin{aligned} G(q, R_{hs}, \phi_{hs}) &= \frac{\alpha}{(2qR_{hs})^2} (\sin(2qR_{hs}) - 2qR_{hs} \cos(2qR_{hs})) \\ &+ \frac{\beta}{(2qR_{hs})^3} (4qR_{hs} \sin(2qR_{hs})) \\ &+ \frac{\beta}{(2qR_{hs})^3} ((2 - (2qR_{hs})^2) \cos(2qR_{hs}) - 2) \\ &+ \frac{\gamma}{(2qR_{hs})^5} (-(2qR_{hs})^4 \cos(2qR_{hs})) \\ &+ \frac{\gamma}{(2qR_{hs})^5} (4(3(2qR_{hs})^2 - 6) \cos(2qR_{hs})) \\ &+ \frac{\gamma}{(2qR_{hs})^5} (4((2qR_{hs})^3 - 6(2qR_{hs})) \sin(2qR_{hs}) + 24) \\ \alpha &= \frac{(1 + 2\phi_{hs})^2}{(1 - \phi_{hs})^4} \\ \beta &= \frac{-6\phi_{hs}(1 + \phi_{hs}/2)^2}{(1 - \phi_{hs})^4} \\ \gamma &= \frac{\phi_{hs}(1 + 2\phi_{hs})^2}{2(1 - \phi_{hs})^4} \end{aligned}$$

#### Notes and references

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