Supporting Information

Enhanced Interfacial Activity of Multi-Arm Poly(Ethylene Oxide) Star Polymers Relative to Linear Poly(Ethylene Oxide) at Fluid Interfaces

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Dynamic Interfacial Tension Reduction



Figure S1. Interfacial tension reduction for 0.05 wt% of PEO stars and linear PEO at (a) air/water interface, and 0.5 wt% of PEO stars and linear PEO at (b) xylene/water and (c) cyclohexane/water interfaces: (\blacklozenge) PEO stars and linear (\Box) PEO 1000k, (\circ) PEO 200k, and (\triangle) PEO 6k.

Surface Tension and Area Oscillation for PEO Star and Linear PEO at the Air/Water Interface

Figure S2 shows examples of the response in air/water surface tension to the perturbation of interfacial area for PEO star and linear PEO adsorbed layers. The surface tension responses for linear PEO are comparable to noise in static measurements. The invariant surface tension responses for linear PEO (Figure S2, a - c) are attributed to fast reconfiguration of polymer chains at the interface, maintaining constant degrees of surface penetration during area oscillation and resulting in nearly zero dynamic dilatational modulus. On the other hand, the PEO star adsorbed layer surface tension oscillated in phase with the oscillating surface area (Figure S2d). This is attributed to the restricted mobility of the highly constrained polymer chains in the multi-arm stars, which hinders their ability to regulate the surface tension during the surface area oscillation. Fast Fourier transforms of the surface tension data during forced surface area oscillations confirms the lack of a dilatational elastic response for linear PEO, while PEO stars demonstrate a strong peak at the frequency of the forced area oscillation.



Figure S2. Surface tension and droplet area oscillation for 0.05 wt% of linear (a) PEO 6k, (b) PEO 200k, or (c) PEO 1000k and (d) PEO stars at the air/water interface. The surface area oscillation frequency is 0.1 Hz. (e) Fast Fourier transform analysis of surface tension response in the dynamic dilatational modulus experiments at the air/water interface: (*) PEO stars and linear (\Box) PEO 1000k, (\circ) PEO 200k, and (Δ) PEO 6k. No peak was detected for linear PEO at the forced oscillation frequency.

Slow Air/Water Surface Compression and Expansion Using Pendant Drop Tensiometer

Surface pressure versus area isotherms were obtained from compression and expansion of PEO star adsorbed layers using the pendant drop tensiometer. An aqueous drop of 0.001 wt% PEO star solution was created and suspended in the air. After the surface tension reached equilibrium, the volume of the drop was decreased at a rate of 0.05 μ L/s, which corresponds to the rate of surface area change of 0.07 – 0.1 mm²/s. Three cycles of surface compression and expansion were recorded.



Figure S3. (a) Surface pressure versus area (mm²) isotherm for PEO stars at air/water interface. The bulk concentration of PEO stars is 0.001 wt%. The surface area compression and expansion rate was kept in the range of $0.07 - 0.1 \text{ mm}^2$ /s. (b) Compression and expansion modulus for PEO stars at air/water interface as a function of surface pressure deduced from the surface pressure versus area isotherm.

Calculation of Static Dilatational Elasticity from Ellipsometry and Pendant Drop Tensiometry

The equilibrium (static) dilatational elasticity is

$$E_{d} = \frac{d\gamma}{d\ln A} = -\frac{d\pi}{d\ln A} = \frac{d\pi}{d\ln\Gamma} = -\frac{d\pi}{d\ln1/\Gamma}$$
(S1)

where γ is the interfacial tension, *A* is the interfacial area, π is the surface pressure and Γ is the surface excess concentration. Ellipsometry provided the static surface excess concentration for each PEO star concentration at which surface pressures were measured in independent experiments. Linear regression for the slope of π vs. ln(1/ Γ) yields a static dilatational elasticity $E_d = 5.1$ mN/m.



Figure S4. Surface pressure area isotherm for PEO stars adsorbed at air/water interface.

Emulsion Stability



Figure S5. Effect of PEO star concentration on emulsion stability: (•) $0.1 (\bullet) 0.05 (•) 0.01 (\bullet) 0.005 (*) 0.001 wt\%$. Changes in height for (a) xylene-in-water and (b) cyclohexane-in-water emulsions at different concentrations of PEO stars as a function of time. Lines serve to guide the eye.





Figure S6. Interfacial tension and droplet area oscillation for 0.05 wt% of (a) linear (a) PEO 6k, (b) PEO 200k, (c) PEO 1000k and (d) PEO stars at the xylene/water interface. The oscillation frequency is 0.1 Hz. (e) Fast Fourier transform analysis of interfacial tension response in the dynamic dilatational modulus experiments at the xylene/water interface: (\blacklozenge) PEO stars and linear (\Box) PEO 1000k, (\circ) PEO 200k, and (Δ) PEO 6k. No peak was detected for linear PEO at the forced oscillation frequency.



Figure S7. Interfacial tension and droplet area oscillation for 0.05 wt% of (a) linear (a) PEO 6k, (b) PEO 200k, (c) PEO 1000k and (d) PEO stars at the cyclohexane/water interface. The oscillation frequency is 0.1 Hz. (e) Fast Fourier analysis of interfacial tension response in the dynamic dilatational modulus experiments at the cyclohexane/water interface: (\diamond) PEO stars and linear (\Box) PEO 1000k, (\circ) PEO 200k, and (Δ) PEO 6k. No peak was detected for linear PEO at the forced oscillation frequency.

Similar to the air/water interface, forced oscillation of the xylene/water or cyclohexane/water interfacial area yielded no response in the interfacial tension for linear PEO, whereas PEO stars produced an interfacial tension oscillation in phase with the forced area oscillation.

Slow Oil/Water Interfacial Compression and Expansion Using Pendant Drop Tensiometer

Surface pressure versus area isotherm were obtained from compression and expansion of PEO star adsorbed layers using the pendant drop tensiometer. An aqueous drop of 0.001 wt% PEO star solution was created and suspended in the oil. After the surface tension reached equilibrium, the volume of the drop was decreased at a rate of 0.05 μ L/s, which corresponds to the rate of interfacial area change of 0.07 – 0.1 mm²/s. Compression and expansion cycles were repeated three times.



Figure S8. Interfacial pressure versus area (mm²) isotherm for PEO stars at (a) xylene/water and (b) cyclohexane/water interface. The concentration of PEO stars in water is 0.001 wt%. The interfacial compression and expansion rate was kept in the range of $0.07 - 0.1 \text{ mm}^2/\text{s}$. In (a), the second and third

cycles are overlapping. Compression and expansion modulus for PEO stars at (c) xylene/water and (d) cyclohexane/water interface as a function of interfacial pressure deduced from the interfacial pressure versus area isotherm.

Analysis for Ellipsometric Determination of Surface Excess Concentration at Air/Water and Oil/Water Interfaces

The surface excess concentration can be calculated from ellipsometrically determined optical properties of an adsorbed layer using the de Feijter relation:¹

$$\Gamma = \frac{d_f(n_f - n_0)}{dn/dc} \tag{S2}$$

where n_0 is the refractive index of the bulk polymer solution, and d_f and n_f are the optical average thickness and refractive index of the adsorbed layer, respectively, and dn/dc is the refractive index increment of the polymer solution, previously reported to be 0.13 cm³/g for both PEO linear and star polymers.²

Here we model the dependence of the calculated surface excess concentration on the assumed refractive index of a PEO adsorbed used when analyzing ellipsometry data. We first generate the ellipsometric parameters for a "true" PEO adsorbed layer using a refractive index of 1.44 and a thickness of 20 Å. These "true" optical properties give a *y* parameter (see main paper, Eqn. 5) according to the homogeneous film striated media optical model that one would obtain experimentally. Then, to mimic the data fitting process, we take an initial guess for the refractive index of the thin adsorbed layer (n_f), fit for the thickness of the adsorbed layer (d_f) which gives the same *y* parameter, and calculate the surface excess concentration using de Feijter relation.

Figure S9 shows the calculated surface excess concentration (Γ) of a PEO adsorbed at the air/water interface ($n_{water} = 1.333$ and $n_{air} = 1.000$). Varying the initial guess for the refractive index of the adsorbed layer from 1.40 to 1.46 (the latter upper limit corresponding to the refractive index of pure PEO) only changes the surface excess concentration by 10%. This indicates that the errors of assumed and fitted optical properties (n_f and d_f) are mutually compensating. Therefore, the value of $d_f(n_f - n_0)$ is nearly invariant (to within ~10%), meaning the surface excess concentration calculated by de Feijter relation is nearly independent of the optical properties of the adsorbed layer at the air/water interface, and quantitative comparisons can be made with ~ 10% tolerance for uncertainty.



Figure S9. Calculated surface excess concentration as a function of the guessed refractive index of the adsorbed PEO layer at the air/water interface, based on analysis of the ellipsometric *y* parameter for the "true" adsorbed layer that has refractive index of 1.44 and thickness of 20 Å. The angle of incidence is 53°.

For PEO adsorption at the xylene/water interface, we follow the same modeling procedure as in the air/water system by assuming the "true" adsorbed layer has refractive index of 1.44 and thickness of 20 Å. As illustrated in Figure S10, the modeling results show that the surface excess concentration of PEO at the xylene/water interface is highly dependent on the value of the guessed refractive index used when analyzing ellipsometric data. The difficulty of obtaining the accurate value of the surface excess concentration results from the weaker optical contrast between the xylene and water phases ($n_{water} = 1.333$ and $n_{xylene} = 1.500$), making the ellipsometric signals less sensitive to the local variation of refractive index caused by the adsorbed layer. In other words, the uncertainly of fitting the experimental data for the optical properties of the adsorbed thin film is large, making it impossible to unambiguously determine the surface excess concentration.



Figure S10. Calculated surface excess concentration as a function of the guessed refractive index of the adsorbed PEO layer at the xylene/water interface, based on analysis of the ellipsometric *y* parameter for the "true" adsorbed layer that has refractive index of 1.44 and thickness of 20 Å. The angle of incidence is 43° .

Turbidity of Spontaneous Emulsion Phase as a Function of PEO Star Concentration



Figure S11. Optical density of the xylene phase of the xylene/water system 3.5 hours after sample preparation. PEO stars were initially dispersed in xylene. Turbidity increased with the bulk concentration of PEO stars initially dispersed in xylene, indicating increasing spontaneous emulsification of water into xylene.

Photographs of Xylene/PEO-Water, PEO-Xylene/Water, and PEO-Xylene/PEO-Water

Table S1. Photographs of xylene/water with 0.1 wt% PEO stars initially dispersed in water (bottom phase), initially dispersed in xylene, and initially dispersed in both xylene and water phases with the same total amount of PEO stars (50/50 mass in each phase)

	Initial	1 h	2 h	3 h	4 h	17 h	24 h
PEO stars in water							
PEO stars in xylene							
PEO stars in water and xylene							

Determination of PEO Partitioning between Xylene and Water: Refractive Index Measurements for Xylene/PEO-Water and PEO-Xylene/Water Systems

A sample was made at a 1:1 xylene/water volume ratio with high concentration of linear PEO 6k in the water phase (33 wt%) and no PEO in the xylene phase. The refractive indices of both xylene and water phases were measured immediately after sample preparation and a week after the preparation. As shown in Table S2, we observed no change in refractive index, indicating that almost all PEO stayed in the water phase instead of diffusing into the xylene phase.

Table S2. Change in refractive index of xylene and water phases in xylene/PEO-water system

Refractive index	Xylene	PEO-water (33 wt%)
At initial time	1.4946	1.3801
After a week	1.4947	1.3808

Another sample with 1:1 xylene/water volume ratio with high concentration of linear PEO 6k (0.10035 g/mL of PEO 6k in xylene) initially in the xylene phase was prepared, with no PEO in the water. The partitioning of PEO 6k between xylene and water phases was examined by measuring the refractive index, as shown in Table S3. The increase in refractive index of the water phase indicates that some of PEO 6k in the xylene phase diffused into the water phase. The redistribution of PEO 6k is due to the greater solubility of PEO in water than in xylene phase.

Table S3. Change in refractive index of xylene and water phases in PEO-xylene/water system

Refractive index	PEO-xylene (10 wt%)	Water
At initial time	1.4958	1.3326
After a day	1.4954	1.3445

The refractive index of water phase, 1.3445, indicates that the final concentration of water phase was 0.091 g/mL. Thus, the partition coefficient for PEO 6k between water and xylene can be calculated

$$P_{water/xylene} = \frac{0.091}{0.10035 - 0.091} = 9.73 \tag{S3}$$

References

- S1 J. De Feijter, J. Benjamins and F. Veer, *Biopolymers*, 1978, **17**, 1759–1772.
- S2 T. Saigal, J. K. Riley, P. L. Golas, R. Bodvik, P. M. Claesson, K. Matyjaszewski and R. D. Tilton, *Langmuir*, 2013, 29, 3999–4007.