



Negative interfacial energies of dynamic polymer brush interfaces: a discussion of the free energy balance

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Abstract

Interfacial energy is an important physical parameter for describing interfacial properties. However, quantifying the interfacial energy of a polymer–liquid interface is extremely difficult because numerous polymers reconstruct when exposed to liquids. A dynamic polymer brush is a reconstructed surface. When a hydrophobic elastomer containing amphiphilic block copolymers comes into contact with water, the copolymers spontaneously segregate at the elastomer–water interface to form a hydrophilic brush known as a dynamic polymer brush. We previously succeeded in analyzing the interfacial energy of a dynamic polymer brush interface by measuring the deformation of an ultrathin square elastomer film floating on water. However, the quantitativity remains debatable because the elastic modulus of a bulk elastomer sheet, rather than an ultrathin elastomer film, was used. In this study, we reanalyze the interfacial energy of a dynamic polymer brush system using the ultrathin-film modulus, which we recently measured via a film-on-water tensile test. Large negative interfacial energy was observed for the system of high-density stretched brushes. The free energy balance for the dynamic polymer brush system floating on water was calculated, and results validated the negative interfacial energy, which is a distinctive feature of dynamic polymer brushes.

The structure and properties of polymer interfaces are closely related to their performance, such as wettability, anti-fouling behavior, and lubricity [1]. Interfacial energy is an important physical parameter for describing interfacial properties. However, quantitatively measuring the interfacial energy of a polymer–liquid interface is difficult because numerous polymers reconstruct when they are in contact with liquid. The interfacial energy can be estimated indirectly using the contact angle method based on Young's equation [2–6]. However, the local surface structure of the reconstructed polymer surfaces changes in presence of droplets, resulting in an inhomogeneous surface in the

nonequilibrium state around the contact line. Therefore, Young's equation is no longer valid [7].

Dynamic polymer brushes are reconstructed polymer surfaces [8, 9]. When an elastomer matrix containing amphiphilic block copolymers with glass transition temperatures below room temperature comes into contact with water, the copolymers spontaneously segregate at the elastomer–water interface to form a dynamic polymer brush. The key driving force is the large increase in the hydration energy of hydrophilic blocks. The interfacial energy is expected to be greatly reduced due to the highly stretched, high-density hydrophilic brushes that spontaneously fill the hydrophobic elastomer/water interface [10]. However, quantitative measurements are difficult owing to the complex dynamics of contact with water [9].

In our previous study, a novel method was proposed to directly evaluate the interfacial energy by measuring the deformation of an ultrathin square elastomer film floating on water [11]. Ultrathin elastomer films are sufficiently soft to be deformed by small forces, such as the surface and interfacial energies. The stress σ_{eng} working on an ultrathin elastomer film with a film thickness d floating on water can be expressed as $\sigma_{\text{eng}} = (\gamma_{\text{L}} - \gamma_{\text{S}} - \gamma_{\text{SL}})/d$, where γ_{L} , γ_{S} , and γ_{SL} are the surface energies of water, the elastomer, and

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the interfacial energy between the elastomer and water, respectively. Assuming that ultrathin square elastomer films floating on water deform equibiaxially according to a neo-Hookean model, the interfacial energy can be expressed as $\gamma_{SL} = \gamma_L - \gamma_S - 2dE(\lambda - \lambda^{-5})/3$, where E and λ are the Young's modulus and elongation ratio of the ultrathin film, respectively. Because γ_L and γ_S are constant, and E and d can be measured by tensile tests and spectrometric ellipsometers, respectively, γ_{SL} can be determined by measuring the deformation of the ultrathin elastomer film.

In our previous report, polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS, 14 wt% PS) and poly(1,4-isoprene)-*b*-poly(ethylene glycol) (PI-*b*-PEG) were used as hydrophobic elastomers and amphiphilic block copolymers, respectively [11]. Two types of PI-*b*-PEG were used with molecular weights of 18500-*b*-6500 (I18E6) and 6500-*b*-16500 (I6E16) g/mol. Square SIS films with a thickness of 170 nm containing 0–25 wt% copolymer were prepared for interfacial energy analysis. For the I18E6 system with shorter hydrophilic PEG chains, the interfacial energy decreased only slightly because of the small gain in the hydration energy associated with the formation of low-density collapsed brushes. However, for the I6E16 system with longer hydrophilic chains, the interfacial energy decreased significantly to zero owing to the large gain in hydration energy associated with the formation of high-density stretched brushes.

Although we successfully measured the interfacial energy of a dynamic polymer brush, its quantitativity remains controversial. We calculated the interfacial energy from the deformation of the ultrathin film using the elastic modulus of the bulk SIS (1 MPa), which may differ from the elastic modulus of the ultrathin films [12]. We recently reported on the stiffening of ultrathin styrene-based thermoplastic elastomer films [13, 14]. For ultrathin SIS films with 14 wt% PS, increases in modulus and unusual relaxation behavior were observed, which may have been attributed to complex factors, including PS domain alignment, confinement effects, and surface and interface effects [14]. Therefore, in our previous study, the decrease in the interfacial energy was underestimated because the actual modulus of the ultrathin SIS film was greater than the bulk modulus used to calculate the interfacial energy [11].

In this study, we reanalyzed the interfacial energy of a dynamic polymer brush system in which PI-*b*-PEG was mixed with an ultrathin SIS film using the ultrathin-film modulus obtained by a film-on-water tensile test. We confirmed that the interfacial energy had a large negative value for a system in which high-density stretched brushes formed. Furthermore, we considered the free energy balance for the dynamic polymer brush system floating on water, which validated the negative interfacial energy.

The characteristics of dynamic polymer brushes formed with I18E6 and I6E16 were discussed in our previous report

[11]. Briefly, a low-density collapsed brush was formed with I18E6 (graft density: 0.27 chains/nm², brush elongation: 0.89), while a high-density stretched brush was formed with I6E16 (graft density: 0.77 chains/nm², brush elongation: 2.4), as determined by neutron reflectometry (NR). The brush elongation is defined as the ratio of the brush height to twice the radius of gyration.

The time-dependent area of the ~170-nm-thick square SIS films floating on water containing 0–25 wt% copolymers was provided in our previous report [11]. We employed the fully relaxed modulus of 170-nm-thick SIS films (9.2 MPa) obtained by the stress relaxation test to calculate the interfacial energy from the deformation extent of the samples because the elastic modulus of the ultrathin SIS film depended on both the film thickness and strain rate (details provided in Supplementary Information) [14]. Fig. 1 plots the recalculated interfacial energy versus the volume of the PEG component of the block copolymer added to the film per unit initial area. The normalized amount of copolymer, d_{PEG} , was defined as $d_{\text{PEG}} = d \cdot c \cdot M_{\text{PEG}} / (M_{\text{PI}} + M_{\text{PEG}})$, where d , c , M_{PI} , and M_{PEG} are the film thickness, copolymer concentration in the film, and molecular weights of the PI and PEG blocks, respectively [11]. The solid black vertical lines in Fig. 1 correspond to the amounts required to reach the equilibrium brush structure described above. Thus, the system did not contain a sufficient amount of copolymer in the region to the left of the line but contained an excessive amount in the region to the right of the line. For the I18E6 system, the interfacial energies decreased slightly and remained positive even when an excessive amount of the copolymer was added (Fig. 1a). In contrast, for the I6E16 system, the interfacial energies significantly decreased and became negative when an excessive amount of the copolymer was added (Fig. 1b). The substantial negative interfacial energies were notable. In general, an interface with a negative interfacial energy is unstable and transforms into a single homogeneous phase as the free energy continues to decrease with increasing interfacial area [15]. However, in a dynamic polymer brush system, the interfacial area does not expand infinitely owing to the elastic energy of the elastomer film. Thus, a negative interfacial energy can be realized.

To discuss the validity of the negative interfacial energy from a thermodynamic perspective, we calculated the free energy balance, ΔF , of the dynamic polymer brush system. We first considered the system mounted on a substrate. In this situation, the ultrathin elastomer layer is never distorted, thus maintaining the constant area of the elastomer–water interface. With brush formation, the system gains hydration energy, F_{hyd} , of the PEG chains but loses stretching energy, F_{str} , of the PEG and PI chains and excluded volume repulsion, F_{rep} , of the PEG chains (Fig. 2a) [8, 16]. To calculate F_{hyd} , we used the mixing

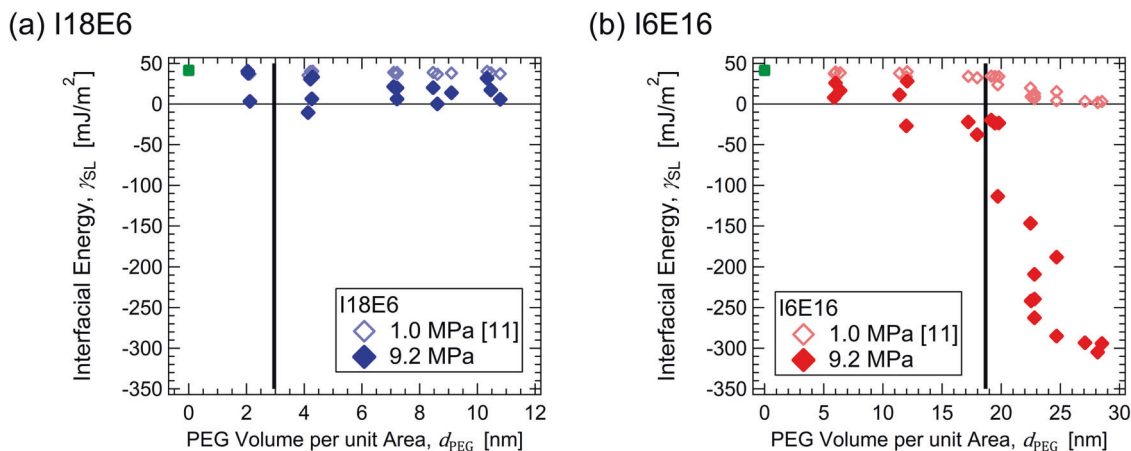


Fig. 1 Interfacial energies of ultrathin polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS) films with (a) I18E6 and (b) I6E16 plotted against the volume of the poly(ethylene glycol) (PEG) component of the block copolymer added to the film per unit initial area. The open and closed rhombuses correspond to the data calculated using the bulk modulus

(1.0 MPa, original data) and the fully relaxed modulus of 170-nm-thick SIS films (9.2 MPa, recalculated data), respectively. The solid black lines correspond to the volume of PEG per unit area required to reach the equilibrium brush structures. Reproduced with permission from ref. [11]

enthalpy of the PEG400–water system, ΔH_{mix} , obtained experimentally using a reaction-solution calorimeter [17],

$$F_{\text{hyd}} = \left(\frac{M_{\text{PEG}}}{N_{\text{av}}} \right) \cdot \Delta H_{\text{mix}}, \quad (1)$$

where N_{av} is Avogadro's constant. To calculate F_{str} , we assumed that the stretching of the chain was described by the Langevin function [8, 18]. F_{str} can be obtained by integrating the inverse Langevin function as follows:

$$F_{\text{str}} = k_{\text{B}}T \cdot (N_{\text{PEG}} + N_{\text{PI}}) \cdot \left[\frac{h}{L_{\text{max}}} \cdot L^{-1} \left(\frac{h}{L_{\text{max}}} \right) - \ln \left\{ \sinh L^{-1} \left(\frac{h}{L_{\text{max}}} \right) \right\} + \ln \left\{ L^{-1} \left(\frac{h}{L_{\text{max}}} \right) \right\} \right], \quad (2)$$

where h is the brush height, L_{max} is the contour length of the chain, k_{B} is the Boltzmann constant, T is the temperature, and N_{PEG} and N_{PI} are the numbers of Kuhn monomers in the PEG and PI blocks, respectively. The conformation of the PI chains embedded in the elastomer could not be analyzed using NR. For simplicity, we assumed that the elongations of the PEG and PI blocks were identical [8]. Furthermore, F_{rep} is given by:

$$F_{\text{rep}} = k_{\text{B}}T \cdot \frac{b_{\text{PEG}}^2 a_{\text{PEG}} N_{\text{PEG}}^2 \sigma}{h}, \quad (3)$$

where b_{PEG} and a_{PEG} are the Kuhn monomer length (1.1 nm) and diameter (0.36 nm) of the PEG chain, respectively [16, 18, 19]. Because we assumed that water is an athermal solvent for PEG for simplicity, the excluded volume repulsion may have been overestimated. The most stable

brush structure was determined by the free energy per unit area as follows:

$$\Delta F = \sigma \cdot (F_{\text{hyd}} + F_{\text{str}} + F_{\text{rep}}), \quad (4)$$

where σ is the chain density. Figure 3 shows the calculated ΔF values as a function of h/L_{max} and σ at 298 K. The most stable brush structure estimated from the calculation was denser and more stretched than the brush structure determined by NR. This could be attributed to an underestimation of free energy losses, such as entropy loss and excluded volume repulsion of PI chains segregated at the elastomer–water interface. Nevertheless, the calculated values were qualitatively consistent with the measured values.

Next, we considered the free energy balance of the system floating on water. In this case, the strain energy of the film, F_{film} , must be considered as the ultrathin SIS film was deformed (Fig. 1b). Here, we assumed that the ultrathin square film deformed equibiaxially according to a neo-Hookean model because the deformation extent was small ($\lambda < 1.06$). The strain energy function W for the equibiaxial deformation was expressed as,

$$W = \frac{G}{2} \cdot (2\lambda^2 + \lambda^{-4} - 3), \quad (5)$$

where G is the shear modulus [20]. Poisson's ratio was assumed to be 0.5, and $G = E/3$. Therefore, F_{film} was given by:

$$F_{\text{film}} = \frac{E}{6} \cdot (2\lambda^2 + \lambda^{-4} - 3) \cdot V, \quad (6)$$

where V is the volume of the ultrathin film. In the interfacial energy analysis, the initial area and thickness of the sample

were $15 \times 15 \text{ nm}^2$ and approximately 170 nm, respectively [11]. These values were used to calculate the free energy. Furthermore, we employed Young's modulus of the 170-nm-thick SIS film (9.2 MPa), which was determined by a

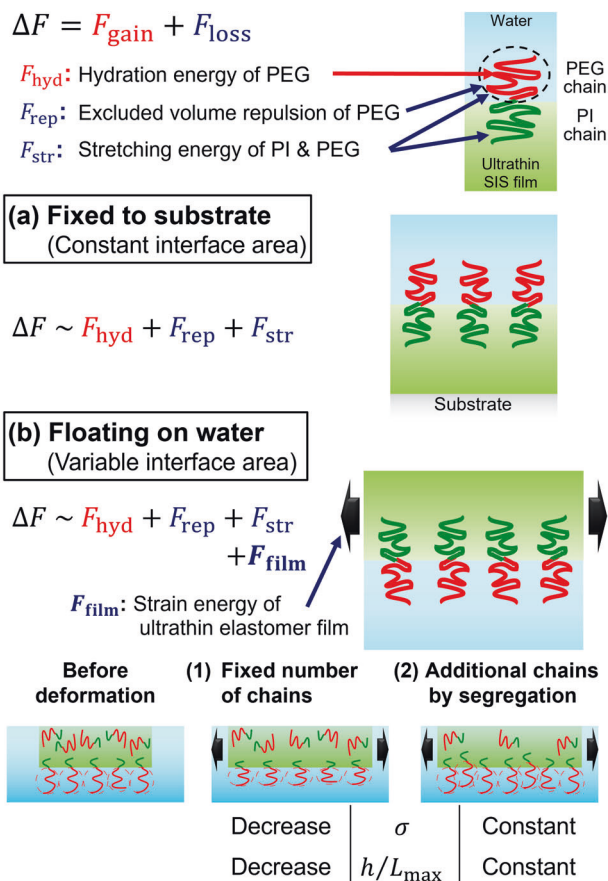


Fig. 2 Schematic of the free energy balance of the dynamic polymer brush system (a) fixed to a substrate (constant interfacial area) and (b) floating on water (variable interfacial area)

stress relaxation test [14]. The brush density and elongation were slightly less for the system floating on water than for those fixed to the substrate according to our previous NR analysis [11]. Therefore, we considered two cases of change in the brush structure with film deformation: (1) a fixed number of chains (variable brush structure), and (2) additional chains by further segregation (fixed brush structure), as shown in Fig. 2b.

In case (1), the copolymers remaining in the ultrathin film cannot segregate to the newly generated interfacial area, that is, the chain density σ decreases to $\sigma\lambda^2$ with film expansion. Assuming that the volume fraction of PEG in the brush layer was constant, hL_{max} also decreased to $(hL_{\text{max}})\lambda^2$, thus decreasing F_{str} . In this case, the system loses the strain energy of the ultrathin film without a gain in the hydration energy as the film expands. This case corresponds to the upper limit of the free energy. The free energy of case (1) can be described as follows:

$$\Delta F = (\sigma/\lambda^2) \cdot (F_{\text{hyd}} + F_{\text{str}} + F_{\text{rep}}) \cdot S_i + F_{\text{film}} + (\gamma_S - \gamma_L) \cdot (\lambda^2 - 1) \cdot S_i. \quad (7)$$

S_i is the initial area of the ultrathin film ($15 \times 15 \text{ nm}^2$) [11]. The last term describes the contributions of the surface energies of SIS (γ_S) and water (γ_L) associated with the change in the SIS–water interfacial area. The surface energy term is smaller compared with that of the other components.

In case (2), the copolymers remaining in the ultrathin film can segregate to the newly generated interfacial area to maintain the equilibrium brush structure; that is, the brush density and elongation do not change with film expansion. In this case, the system loses strain energy with film expansion but gains hydration energy with further brush formation. This case corresponds to the lower limit of free energy. The free

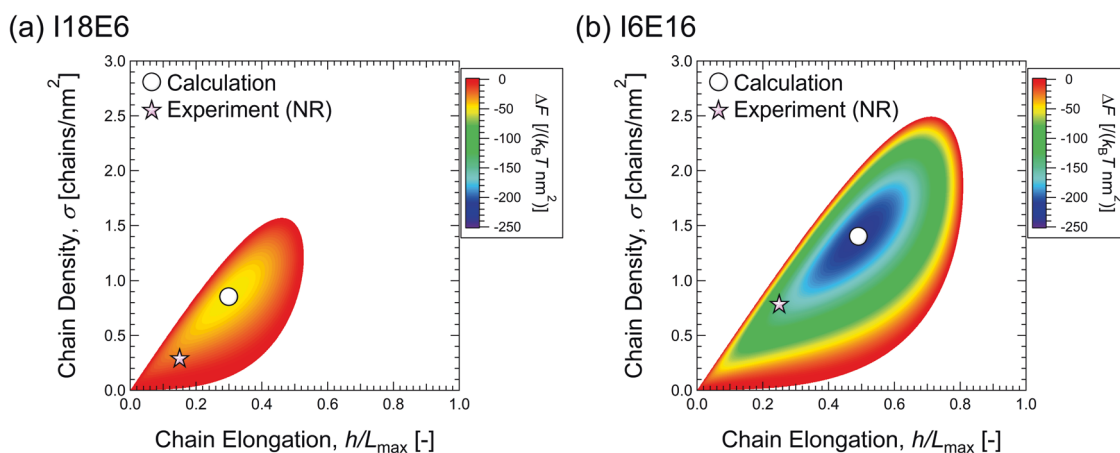


Fig. 3 Calculated free energy per unit area as a function of chain elongation hL_{max} and chain density σ for the system with (a) I18E6 and (b) I6E16 fixed to a substrate (constant interfacial area). The white

circles and pink stars correspond to the most stable brush structure estimated from the free energy calculation and the brush structure determined experimentally by neutron reflectometry, respectively

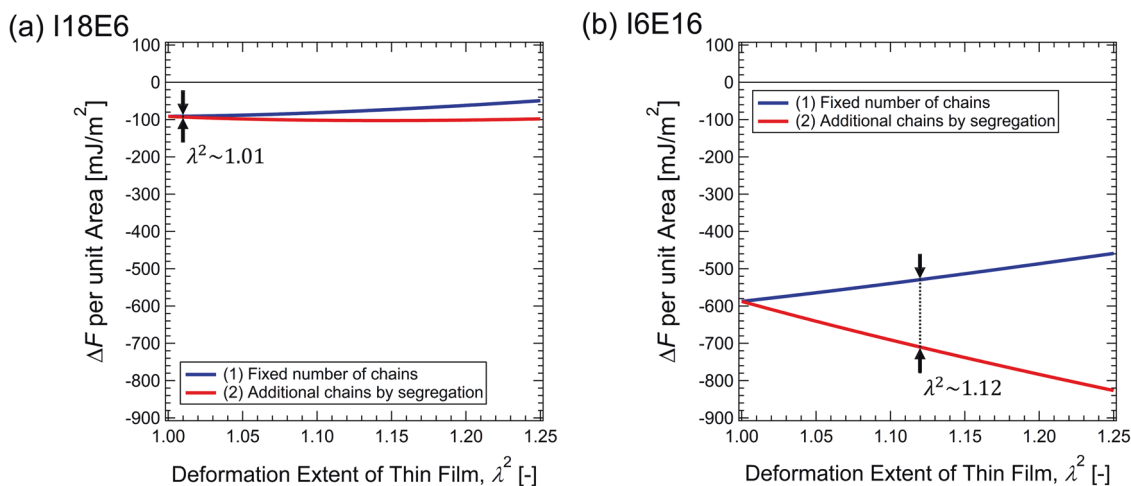


Fig. 4 Calculated free energy with film deformation for the ultrathin SIS films with (a) I18E6 and (b) I6E16 floating on water (variable interfacial area). The blue and red lines correspond to the results of calculations for the cases with (1) a fixed number of chains

and (2) additional chains by further segregation, respectively. The black arrows indicate the extent of the film deformation measured experimentally

energy for case (2) can be described as follows:

$$\Delta F = \sigma \cdot (F_{\text{hyd}} + F_{\text{str}} + F_{\text{rep}}) \cdot \lambda^2 S_i + F_{\text{film}} + (\gamma_S - \gamma_L) \cdot (\lambda^2 - 1) \cdot S_i. \quad (8)$$

In a real system, the free energy should be between those of the two cases. Figure 4 summarizes the results of the free energy calculations for the system floating on water. The calculations employed the chain density (0.27 and 0.77 chains/nm² for I18E6 and I6E16, respectively) and chain elongation hL_{max} (0.15 and 0.25 for I18E6 and I6E16, respectively) determined by NR. The free energy was divided by the interfacial area for simple comparison with the interfacial energy. For the I18E6 system, the free energy decreased only slightly with film expansion, even when additional copolymers segregated to the newly generated area (Fig. 4a (2)). Although the free energy reached a minimum value at $\lambda^2 = 1.14$, the decrease in free energy was limited. This indicated that the gain in the free energy associated with the formation of the low-density and collapsed brush was smaller compared to the strain energy of the film. In particular, the expansion of the interfacial area was unfavorable, and hence, the interfacial energy remained positive for the I18E6 system. In contrast, for the I6E16 system, the free energy decreased significantly with further brush formation as the film expanded (Fig. 4b (2)). The large decrease in free energy was derived from the large gain in hydration energy associated with the formation of high-density stretched brushes (Fig. 3b). This system could overcome the strain energy of the ultrathin elastomer film to expand the interfacial area, leading to a negative interfacial energy. Notably, the ultrathin SIS film did not expand infinitely because the strain energy of

the film could be balanced with the negative interfacial energy. Possible reasons for the finite expansion of a real system were the lack of copolymers in the system that could form additional brushes to increase the hydration energy and the increased strain energy of the ultrathin elastomer film with a large deformation compared to the gain in hydration energy with additional brush formation. Another possible reason was that the free energy gain associated with brush formation in the calculation is overestimated (Fig. 3). We have not been able to identify the factors that cause the discrepancies between the experimental and calculated results. Nevertheless, it is worth noting that the calculated free energy gain per unit area (from -550 to -700 mJ/m²) was close to the measured interfacial energy value (-300 mJ/m²). These free energy calculations qualitatively supported the large negative interfacial energy realized explicitly in the dynamic polymer brush system.

In summary, the interfacial energy became a large negative value for the dynamic polymer brush system in which high-density stretched brushes were formed. To discuss the validity of the negative interfacial energy from a thermodynamic perspective, we calculated the free energy balance for a dynamic polymer brush system fixed to a substrate (constant interfacial area) and floating on water (variable interfacial area). The results suggested that a negative interfacial energy could be realized when the free energy gain with brush formation was sufficiently large compared to the strain energy associated with film expansion. Negative interfacial energy is a unique property of the dynamic polymer brush system in which hydrophilic brush layers spontaneously form at the cross-linked elastomer–water interface.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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