“Loop” or “Tail”? Self-Assembly and Surface Architecture of Polystyrene-graft-ω-stearyl-poly(ethylene oxide)

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To investigate the possibility of engineering a glycocalyx-like surface via end-tethered hydrophobic ligand onto poly(ethylene oxide) (PEO), polystyrene-graft-ω-stearyl-poly(ethylene oxide) (PS-g-SPEO), which has poly(styrene) backbone and PEO side chains end-functionalized with stearyl groups, was specifically prepared. X-ray photoelectron spectroscopy results indicated that SPEO was enriched at the surface. Differential scanning calorimetry results revealed that the stearyl end groups tended to assemble a stable stearyl phase, which could be destroyed by a thermal treatment. A “looplike” SPEO (sample A) and a “tail-like” SPEO (sample B), which had almost the same surface composition, were then used as model surfaces to study the surface architecture of end-tethered PEO in aqueous environment. The contact angle at the sample A/water interface decreases rapidly with increasing of the water hydration time. After longer water incubation, it presented a hydrophilic interface with the low PEO mobility. Sample A was shown to impart significant resistance to both albumin and fibrinogen adsorption. But it is nonselective for the albumin. By contrast, the contact angle at the sample B/water interface decreases little with water hydration. It presented a hydrophobic interface with the high ethylene oxide mobility. Sample B exhibits a very low fibrinogen adsorption while adsorbing a high level of albumin. All above results proved that sample B may keep a “tail-like” SPEO in aqueous solution and is possible to get a glycocalyx-mimetic surface, in which a hydrophobic matrix was covered by a layer of flexible hydrophilic PEO and then by hydrophobic signal molecules.

Introduction

The external region of a cell membrane, known as the glycocalyx, is dominated by glycosylated molecules, which direct specific interaction such as cell—cell recognition and contribute to the steric repulsion that prevents undesirable nonspecific adhesion of other molecules and cells. The densely packed, highly hydrated polysaccharides provide a physical basis for maximizing entropic repulsion and prevent nonspecific adhesion. Desirable adhesive interaction and biological specificity are often achieved through the specific interaction between cell-surface glycoprotein receptor molecules (including hydrophilic ligand and hydrophobic ligand). In following this biological perspective, investigators have been stimulated to explore the engineering of poly(ethylene oxide) comblike copolymers as glycocalyx-mimic surfaces. The comblike PEO chains have been regarded as the most effective structures to reduce the nonspecific interaction and they can be end-tethered ligands to obtain specific cell—substrate interactions. It allows, in general, biomimetic engineering of a glycocalyx-like surface (Scheme 1).

Several groups have succeeded in immobilizing a hydrophilic ligand via a PEO “spacer” to get a highly specific surface. But is it possible to get a glycocalyx-like surface via end-tethered hydrophobic ligand onto PEO? Will the hydrophobic ligands bend over to get “loop” structure or present “tail” architecture in aqueous environment (Scheme 2)?

To get insight of this question, polystyrene-graft-[ω-stearyl-poly(ethylene oxide)] (PS-g-SPEO), which has poly(styrene) backbone and poly(ethylene oxide) side chains end-functionalized with stearyl groups, is specifically prepared. Self-assembly and surface structure of PS-g-SPEO were characterized by X-ray photoelectron spectroscopy (XPS), differential scanning calorimeter (DSC), electron spin resonance spectroscopy (ESR), and contact angle techniques. The competitive adsorption from the 125I-labeled fibrinogen and unlabeled albumin (or 125I-labeled albumin and unlabeled fibrinogen) was investigated to assess the possibility of engineering surfaces with high specific to albumin.

Experimental Section

Materials. The stearyl-poly(ethylene oxide) (SPEO) grafted copolymers were synthesized by free radical copolymerization of styrene monomer with acryloyl SPEO macromonomer. The structure of the graft copolymers was determined by FT-IR (FTIR-50x) and 'H NMR (FX-90Q), and their number-average-molecular weight (Mn) and the molecular weight distribution (MWD) were measured by vapor pressure osmometry (VPO) (Knauer VPO) and gel-permeation chromatography (GPC) (Waters-208), respectively (Table 1). The comblike structure can be illustrated as Scheme 3.

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of 1,4-hydroxyl-TEMPO in water. Samples were maintained at
temperature for 24 h before washing extensively to remove
any surface-bonded spin probe. ESR measurements were made
on a J ES-Fixing (J EOL) spectrometer. Samples were introduced
into the cavity in a cylindrical glass tube, with a diameter of 5
mm. Spectra were recorded using the following instrumental
parameters: scan range 250 G; time constant 0.3 s; scan time
4 min; modulation amplitude 1 G; microwave power 4 mW; each
sample was measured three to five times for reproducibility.
The parameters of the ESR spectra were measured in comparison
with those of Fremy’s salt. (Nitrogen hyperfine constant \( a_N =
13.0 \text{ G} \).) The rotational correlation time \( \tau_c \) was calculated with
the following formula:

\[
\tau_c = (6.51 \times 10^{-10}) \Delta H(0) \left( \frac{[h(0)/h(1)]^{1/2} - [h(0)/h(1)]^{1/2}}{2} \right)
\]

where \( \Delta H(0) \) is the line width (in G) of the central line, \( h(0),
\) \( h(1), \) and \( h(+1) \) are the peak heights of
m, 0, and +1 derivative lines, respectively (15).

**Protein Adsorption.** The protein adsorption experiment
utilized surfaces in the form of tubing segments of diameter in
the range from 2 to 4 mm. The surfaces for protein adsorption
were prepared by solution coating from 0.5% w/v solution of the
polymer in ECL on inside of glass tubes (diameter 3 mm). The
sample A was dried at room temperature and in a vacuum
overnight. Sample B was prepared by the same procedure
following thermal treatment, in which it was heated to 60 °C
and cooled at \(-25 \text{ °C/min}. \) All surfaces were characterized by electron
microscope examination to confirm no flaw at polymer
membranes.

Human serum albumin was from Sigma and was 97%
electrophoretically pure. Human fibrinogen was from Sigma
and was 95% of table. Albumin and fibrinogen were labeled by iodine-125
using the iodine monochloride technique as described by
Brash. (13) Experiments were conducted to verify no dependence
of the measured surface concentration on percentage of labeled
protein over a range of 1–20% in our lab. Amounts of 125I-labeled
protein were added to the diluted plasma or buffer to give the
mixtures containing 5% labeled and 95% unlabeled protein.

The preferential binding of albumin by modified and unmodi-
ified surfaces was determined by using the mixtures of 125I-labeled
albumin and fibrinogen (or 125I-labeled fibrinogen and albumin).
Fibrinogen was used as a competitive protein because it is known
to readily absorb to implant surface and because surfaces that
avidly adsorb fibrinogen may be highly thrombogenic. Tubes were
exposed to 125I-labeled albumin/fibrinogen or 125I-labeled fibrinogen/albumin mixture (albumin 0.4 mg/mL, fibrinogen 0.03 mg/
ml, which is 1% concentration of albumin/fibrinogen in plasma)
for 2 h at 25 °C. The tubes were then displaced by 30 times the
volume buffer. Surface radioactivity was measured in a γ-count
and converted to mass of protein per square centimeter by
comparison with aliquot protein solutions.

At least five experiments were conducted for each set of
conditions. Standard deviations, based on all measurements
considered at steady-state, range from ±10% of the mean at low
surface concentration to ±5% at high surface concentration.

and the molecular structure of the graft copolymers (Table eV. The overlapping C 1s peaks of the graft copolymers O1s core level at 533.2 eV and a single C 1s peak at 286.5 eV. The spectrum of PEO shows a single peak for the weight of styrene repeat unit and SPEO side chains. PS wt % and SPEO wt % are the surface weight percent for weight of styrene repeat unit and SPEO side chains. PS

Results and Discussion

Assembly at Polymer/Air Interface. The surface chemical compositions of the films were studied by XPS. The spectra of PS-g-SPEO exhibit one single peak for the O1s core level at 533.2 eV and one overlapping peak for the C 1s core level. To establish a firm basis for the interpretation of the graft copolymer data, the component homopolymers, PS, n-octadecane, and PEO, were investigated to determine their binding energies (E_b). The spectra of PS and n-octadecane have a strong peak centered at 285 eV. The spectrum of PEO shows a single peak for the O1s core level at 533.2 eV and a single C 1s peak at 286.5 eV. The overlapping C 1s peaks of the graft copolymers were then resolved into their individual components by means of the software dedicated in the XPS spectrometer: a C1s-A peak at 285 eV for both PS and stearyl, and a C1s-B peak at 286.5 eV for PEO. Accordingly the area ratio C1s-A/C1s-B was obtained, and the surface SPEO content can be derived from the value of area(C1s-A/C1s-B) and the molecular structure of the graft copolymers (Table 2):

For PS-g-SPEO, the SPEO sidechain is C_{18}H_{37}O-(CH_{2}-CH_{2}O)_{33}-

\[
\text{area(C1s-A/C1s-B)} = \frac{\text{number of C in PS and stearyl}}{\text{number of C in PEO}}
\]

\[
\text{PS wt \%M_{n}(styrene)} \times 8 + \text{SPEO wt \%M_{n}(SPEO)} \times 18 = \text{SPEO wt \%M_{n}(SPEO)} \times 33 \times 2
\]

(2)

where M_{n}(styrene) and M_{n}(SPEO) are the molecular weight of styrene repeat unit and SPEO side chains. PS wt \% and SPEO wt \% are the surface weight percent for PS and SPEO, respectively.

As PS wt \% + SPEO wt \%= 1, the eq 2 can be simplified as

\[
\text{SPEO wt \%} = \frac{[M_{n}(SPEO) \times 8]/[M_{n}(SPEO) \times 8 + M_{n}(styrene) \times \text{area(C1s-A/C1s-B)} \times 33 \times 2]}{M_{n}(styrene) \times 18}
\]

As shown in Table 2, SPEO enriches at the PS-g-SPEO/air interfaces. Both surfaces are almost covered by SPEO.

This is not surprising if we examine the data with respect to the surface migration behavior on the copolymer/air interface. The critical surface tensions of n-octadecane, PS, PEO, and ECL (M_n = 6000) are 27.87, 42, 45.9, and 36.36 in mN/m, respectively. Therefore, it is expected that, in an attempt to achieve the lowest interfacial energy, the stearyl will migrate and accumulate at the surface. As the stearyl end groups covalently bind with PEO side chains, the motion of the stearyl can force the flexible PEO chain to move with it in the same direction. The mutual movement restriction between the stearyl and PEO is supposed to be rather strong, which means that the PEO chains can be constrained to remain in the water interface.

Restructure and Surface Architecture at the Polymer/Water Interface. In an aqueous environment, the PEO molecules will achieve their minimum free energy by binding water molecules to the ether groups (exothermic) and diffusing into the water phase to achieve as random (high entropy) conformations as possible. The surface rearrangement was investigated by contact angle. Sessile drop experiment data are reported in Figure 2 as a function of the water hydration time.

The contact angle at the sample A/water interface (Figure 2a) decreases rapidly for the first 50 min, which suggests that surface chemical rearrangement is occurring during water contact. After 4 h of incubation in water, the sample A/water interface has a quite low contact angle. The hydrophilic EO component dominates at the polymer/water interface.

The contact angle at the sample B/water interface (Figure 2b) decreases very slowly for the first 10 min and polymer/air interface. Furthermore, since the mobility of the PS segment decreases rapidly with solvent evaporation, the SPEO-enriched surface structure can be frozen into place (Scheme 4).

The DSC curves for the first heating of the films are shown in Figure 1. It is a striking observation that sample A has two transition peaks, T_1 = 29.3 °C, T_2 = 39.7 °C. The peak at 39.7 °C is ascribed to T_m of the PEO by the DSC spectrum of the pure PEO standard, while the peak at 29.3 °C is within the T_m range of octadecane, 28–30 °C (Aldrich catalog 96/97, P 1136). A stable stearyl phase was detected in sample A. Because of the low mobility of the stearyl groups at the liquid crystalline phase, the PEO of sample A is fixed by both glassy state PS and stearyl phase. It presents a “loop” SPEO structure. DSC results indicate that the stearyl phase could be destroyed by a thermal treatment, and then the “tail” SPEO structure could be obtained on sample B.

It is interesting here to convert a “looplike” SPEO (sample A) into a “tail-like” SPEO (sample B) via a control thermal treatment. Since the anneal temperature is lower than the T_m of PS, the mainly change could be ascribed to the restructuring of SPEO. The two different surfaces, which have almost the same surface composition, are valuable to study the surface architecture of end-tethered PEO in an aqueous environment.

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Table 2. The XPS Results of PS-g-SPEO-72.6

<table>
<thead>
<tr>
<th>sample</th>
<th>thermal treatment</th>
<th>C_{12}-A/C_{12}-B</th>
<th>SPEO wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>no</td>
<td>0.35</td>
<td>96.2</td>
</tr>
<tr>
<td>B</td>
<td>yes</td>
<td>0.33</td>
<td>97.2</td>
</tr>
</tbody>
</table>

a Area ratio C_{12}-A peak at 285 eV for both PS and stearyl, and a C_{12}-B peak at 286.5 eV for PEO.

in the PS-EO segment motion on the PS-SPEO surface. The lower \( \alpha_N \) value of the probe, which is highly sensitive to local polarity, was used to check possible associations of the probe. The results (Table 3) show that the \( \alpha_N \) values in the PS-g-SPEO copolymer are 16.53–16.67 G, which correspond to the probe in PEO and SPEO, whereas the \( \alpha_N \) in PS is 26.16 G. The hydrophilic spin probe is strongly biased toward the PEO phase of the PS-g-SPEO membranes. The rotational correlation time \( \tau_c \), which is viewed as the time taken for an axis of the nitroxide group to travel through one radian, can be employed to assess the EO segment motion on the PS-g-SPEO surface. The lower \( \tau_c \) corresponds to the higher EO mobility.

The \( \tau_c \) of spin probe at the sample A/water interface is much less than that at the sample B/water interface, which indicates the SPEO chains at the sample B/water interface present quite high mobility. The architecture of the grafted SPEO chains at the sample B/water interface may be described as a hydrophobic “tail-like” interface with high EO mobility.

### Protein Adsorption

Albumin was found to be “passive” to both platelets and bacteria; i.e., a confluent layer of conformational intact albumin is supposed to be both antithrombogenic and anti-infective. On the basis of the stratagem for the selective binding of albumin to free fatty acid, 16 or 18 carbon alkyl groups were immobilized onto surfaces. Unfortunately, these materials, perhaps due to the nonspecific interaction between proteins and materials, do not have a high degree of selectivity for albumin and may encourage the subsequent denaturation of absorbed protein. The comblike PEO surfaces end-tethered by stearyl group were then designed to get an albumin-selective surface.

The preferential binding of albumin was determined by using the mixtures of \(^{125}\)I-labeled albumin and fibrinogen (or \(^{125}\)I-labeled fibrinogen and albumin). Fibrinogen was used as a competitive protein because it is known to readily absorb to implant surface and because surfaces that avidly adsorb fibrinogen may be highly thrombogenic. Data for the competitive adsorption from the \(^{125}\)I-labeled fibrinogen and unlabeled albumin (or \(^{125}\)I-labeled albumin and unlabeled fibrinogen) buffer are shown in Figure 3. Sample A is shown to impart significant resistance to both albumin and fibrinogen adsorption. However, it still absorbs more fibrinogen than albumin. It is nonselective for the albumin. By contrast, sample B exhibits a very low fibrinogen adsorption while adsorbing a high level of albumin. The highly albumin preferential adsorption surfaces are formed, with ratios of albumin to fibrinogen of 26.3, at the sample B surface.

### Table 3. \( \alpha_N \) and \( \tau_c \) of 4-Hydroxyl-TEMPO in PS-g-SPEO Copolymer Membranes

<table>
<thead>
<tr>
<th>thermal treatment</th>
<th>( \alpha_N ) (G)</th>
<th>( \tau_c ) (°)</th>
<th>EO mobility</th>
</tr>
</thead>
<tbody>
<tr>
<td>sample A</td>
<td>no</td>
<td>16.53</td>
<td>1.16</td>
</tr>
<tr>
<td>sample B</td>
<td>yes</td>
<td>16.67</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Figure 2. Time dependence of sessile drop contact angle of sample A (not thermal treated) (a) and sample B (thermal treated) (b) (at 25 °C, number of repeats \( n = 10 \), standard deviations less than \( \pm 2^{\circ} \)).
Before discussing the protein adsorption behavior onto both surfaces, it is helpful to review the mechanisms of protein rejection by PEO-containing coatings. The ability of PEO coating to reduce the adsorption of proteins has been widely used in biomedical applications. Although the protein-rejecting properties of a PEO-containing coating are well-known, there has been some discussion over the last couple of decades regarding the molecular mechanisms behind this phenomenon, and different hypotheses have been suggested. By now, however, there seems to be an increasing consensus that protein-rejecting properties are due to a combination of different effects and that a steric interaction between protein and PEO layer is particularly important.\(^{20-25}\)

When two polymer-coated particles approach each other, there will be an overlap of polymer coatings between the particles. If the polymer experiences a good solvency condition, the particles will repel each other, a phenomenon referred to as steric stabilizations.\(^{23-25}\) Similarly, for a particle or a protein to be able to adsorb directly at PEO-coated surface, it will have to diffuse through the PEO layer. The compression of these heavily hydrated, flexible PEO will lead to the unfavorable entropy change (\(\Delta S_{\text{PEOComp}}\)). Although the PEO chains are randomly oriented, there is considerable ordering of water around these chains, with two or three waters closely associated with each ethylene oxide unit.\(^{25}\) The negative entropy change upon PEO compression (\(-\Delta S_{\text{PEOComp}}\)) can be compensated by a positive entropy change associated with loss of waters of hydration from the PEO chain (\(\Delta S_{\text{H}_2\text{O}}\)). But there would be a large endothermic enthalpy change opposing this loss (\(\pm \Delta H_{\text{H}_2\text{O}}\)). Thus if water is lost, adsorption is enthalpically unfavorable, and if water is not lost, protein adsorption is entropically unfavorable; in either case the overall free energy change (\(\Delta G_{\text{PEO}}\)) is positive and unfavorable (eq 3). For adsorption to occur, the free energy for interaction of protein with the surface (\(\Delta G_{\text{Ads}}\)) must offset \(\Delta G_{\text{PEO}}\).\(^{25}\)

\[
\Delta G_{\text{PEO}} = +\Delta H_{\text{H}_2\text{O}} - T(\Delta S_{\text{H}_2\text{O}} - \Delta S_{\text{PEOComp}}) \tag{3}
\]

Sample A in aqueous presents “looplike” PEO chains due to the fixation of both glassy state PS and stearyl phase. The “looplike” PEO chains are less mobile than “tail-like” PEO chains and may contribute less in the negative entropy change upon PEO compression (\(-\Delta S_{\text{PEOComp}}\)). But the bending over of PEO chains will increasing interfacial chain density and may contribute more in positive enthalpy change associated with loss of hydrated waters from the PEO chain. The protein adsorption data here indicate the “looplike” PEO chains still impart significant resistance to both albumin and fibrinogen adsorption. The highly dense PEO-covered surface shows nonselective for albumin.

Sample B in aqueous present a hydrophobic surface with high PEO mobility, which we described as a “tail-like” surface architecture above. It is of interest to examine this surface architecture hypothesis with respect to the steric interaction between stearyl groups and PEO layers. As we have mentioned above, the hydrophobic bending of stearyl groups and hydrophobic matrix will be an energetically driven process (\(\Delta G_{\text{bending}}\)). However, when the “tail-like” SPEO chains bend over to the “looplike” chains, the compression of these heavily hydrated, flexible PEO will lead to the unfavorable entropy change (\(-\Delta S_{\text{PEOComp}}\)). The bending over of PEO will induce “over crowding” with the polymer brush, which will result in loss of hydrated waters from the PEO chain. And the positive enthalpy change (\(+\Delta H_{\text{H}_2\text{O}}\)) of the process will far overcome the positive entropy contribution (\(\Delta S_{\text{H}_2\text{O}}\)). In this case, the overall free energy change of SPEO (\(\Delta G_{\text{SPEO}} = +\Delta H_{\text{H}_2\text{O}} - T(\Delta S_{\text{H}_2\text{O}} - \Delta S_{\text{PEOComp}})\)) may offset the free energy for interaction of stearyl with the hydrophobic matrix (\(\Delta G_{\text{Hydrophobic}}\)) (Scheme 5). As a result, a hydrophobic surface with “tail-like” SPEO chains is stabilized by the steric repulsion due to high dynamic motion of the PEO chain. The free stearyl end groups are known to be able to bind the host albumin in the specific adsorption described by the models of “binding sites pockets”\(^{26}\) and “Scatchard plot.”\(^{27}\)

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Simulation 3. Protein competitive adsorption from multicomponent buffer onto sample A (a) and sample B (b). Samples were exposed to \(^{125}\)I-labeled albumin/fibrinogen or \(^{125}\)I-labeled fibrinogen/albumin mixture (fibrinogen 0.03 mg/mL, albumin 0.4 mg/mL, with a molar ratio, fibrinogen to albumin of 0.015, near to values found in plasma) for 4 h, at 25 °C. The samples were then washed by 30 times volume buffer and counted in a \(\gamma\)-counter. Each point represents the average of five experiments with standard deviation from 5.0% to 7.0% within each set.

The success of the protein binding is always based on two dominant preconditions of the exertion of stearyl hydrophobic property and the mobility of this endgroup. Since the SPEO chains keep the heavily hydrated, flexible “tail-like” surface architecture, it inherited the steric repulsion to the nonspecific adsorption of fibrinogen. Furthermore the expending, flexible “tail-like” SPEO provides more opportunity to the “specific” binding between albumin and the stearyl groups.  

The surfaces for attracting binding albumin are then obtained due to the synergistic action of the PEO chains and the stearyl end groups.


**Summary**

SPEO chains were found to self-segregate at the PS-g-SPEO surface due to the self-migration of stearyl groups. The hydrophobic interaction between the stearyl groups is strong enough to form a stable glassy stearyl phase, which can be destroyed by a heat-quenching process. This property was used to design “looplike SPEO” (sample A) and “tail-like surface” (sample B) surface. The surface rearrangement and the surface architecture of both surfaces were then investigated by the contact angle and ESR spin probe technique. Sample A presents a hydrophilic surface with low SPEO mobility, which seems to remain the “looplike” SPEO. By the contrast, sample B presents a more hydrophobic surface with high SPEO mobility, which may be “tail-like”. Once again the selective adsorption of albumin onto sample B suggests that a glycocalyx-mimic surface, in which a hydrophobic matrix was covered by a layer of flexible hydrophilic PEO and then by hydrophobic signal molecules, is possible.

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