Various-sized stearyl poly(ethylene oxide) coupling-polymer blending poly(ether urethane) material for surface study and biomedical applications

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Introduction

According to our published paper,[1] a kind of coupling-polymer MSPEO was designed and synthesized by a simple reaction between stearyl poly(ethylene oxide) (SPEO) and 4,4'-diphenylmethane diisocyanate (MDI). MSPEO can be analyzed in a similar way to SPEO-MDI-SPEO. Using a solution process, the blended films of poly(ether urethane) (PEU) were prepared for medical applications, especially for anti-coagulation. PEU has been widely accepted as the matrix material because of its unique tissue-compatibility and excellent mechanical properties.[12,3] The coupling-polymer MSPEO was used as the surface-modifying additive (SMA) to overcome the relatively poor blood-compatibility of the PEU matrix.[14–7] Thus, the stearyl end groups (C18) can differentially adsorb the albumin, which will also increase the material’s blood compatibility.[8–10] Analysis on the PEO-modified surface was reported by others.[14–18] The stability of this blending was insured by the H-bond linking the middle urethane block (M-block) of MSPEO and the “hard” urethane block of PEU chain segments, as seen in Scheme 1a and 1b.[11] The surface modification was finally accomplished due to a self-motioned mechanism of the SMA’s surface enrichment.[1]

In this paper, three kinds of SPEO with various lengths of PEO chain (Mn 2300, 6000 and 12000) were prepared.
Accordingly, three kinds of MSPEO (MSPEO 2300, 6000 and 12000) were synthesized. After the blending process, these three samples of PEU blending MSPEO films (PEU-MSPEO 2300, 6000 and 12000) were respectively studied at the surface of air interface and water interface. With the \( M_n \) variation of the MSPEOs, the SMA’s behavior of surface enrichment, as well as the blended samples’ surface composition and structure were detected by the characterization of ATR-FTIR, XPS and two methods of contact angle measurements. Finally, a kind of in vitro testing of static blood-compatibility, plasma recalcification time (PRT), was performed, and the longer PRT was acquired on the blended samples.

**Experimental part**

**Materials and synthesis**

1. Preparation of SPEO: First the initiator, sodium salt of stearyl alcohol was synthesized from the flayed sodium (Shao-yun Electric Chemical Factory, China) and stearyl alcohol (Aldrich) in refluxing benzene (Hangzhou Chemical Reagent Factory, China, Purified) at 80°C, in vacuum dried apparatus under a \( N_2 \) atmosphere. Finally the off-white crystalline sodium salt of stearyl alcohol was prepared, and was stored in a desiccator in the presence of \( CaH_2 \) and highly pure nitrogen.

The preparation of SPEO was performed in a stainless steel reactor with the initiator using toluene as the solvent.
The system was dried and filled with N₂. With respect to the conditions of anionic polymerization and the given quantity of the initiator, the amount of EO (Chemical Factory of Zhejiang Univ., China) added was based on the ideal theoretical $M_n$. Three kinds of monomer/initiator ratio were used. The reaction temperature was $110 \sim 125^\circ C$ and the highest pressure was $0.5 \sim 0.6 \text{ MPa}$. When the inner pressure reduced to less than $0.08 \text{ MPa}$, the reaction was complete.

2. Synthesis of MSPEO: According to the three types of synthesized SPEO, three types of amphiphilic coupling-polymer MSPEO were synthesized by the reactions with MDI (YiXing Chemical Factory, China). The molar ratio of SPEO/MDI was 2:1 and the catalyst was di-$n$-butyl tin dilaurate.

3. Blending Process: The PEU material, which was a commercially available biomedical grade material, Pellethane 2363-80AE (PEL; Dow Chemical, USA), was extracted with absolute alcohol in a Soxhlet extractor. According to the process reported by B. Wesslen et al.\cite{15} and our research group,\cite{1} three blended films of PEL-MSPEOs were prepared with MSPEOs and PEL, in which MSPEO was 5% (w/w). They were prepared by solvent casting onto clean Petri dishes from the 12% (PEL-MSPEO/DMF, w/w) DMF solutions. The films were cast in two layers with evaporation of the solvent between each casting (24 h, at $60^\circ C$). Final drying was carried out in a vacuum oven (3 mm Hg) at $60^\circ C$ for 24 h.

Characterization of the material

$^1$H NMR was performed on SPEOs and MSPEOs. Surface analysis was carried out using ATR-FTIR, XPS and contact angle measurements. The samples were PEL-MSPEO 2300, 6000 and 12000 respectively on air interface and water interface, as well as the PEL control.

1. $^1$H NMR: $^1$H nuclear magnetic resonance spectroscopy (500 MHz, AVANCE DMX500, Bruker) was used to obtain the information about the synthesis of SPEO and MSPEO. The $M_n$ of the SPEO samples was obtained from the quantitative analysis of $^1$H NMR with the solvent CDCl$_3$ (Beijing Reagent Factory, China).

2. ATR-FTIR: The attenuated total reflectance – Fourier transform infrared spectroscopy (E.S.P., MAGNA-IR560, Nicolet) was used to analyze the varieties at the surface of the samples. The samples on the water interface were obtained after 24 h of leaching and a quick vacuum drying at room temperature. They were then examined within a short time, which was practically the same for all the samples obtained under the same conditions.

3. XPS: Angle-dependent XPS analysis (ADXPS, VG Instruments) was carried out to semi-quantify the surface composition of the samples (Fig. 1). The pre-treatment of the samples was the same as that of ATR-FTIR. Under a chamber pressure of $<10^{-7} \text{ mbar}$, Mg X-ray was used, and electron flooding was not used to offset the charging. High-resolution scans of the C1s region was acquired and take-off angles (TOA) of 0, 30, 60 and 90° were collected. Due to the complexity of the insulation polymeric PEU matrix and the inevitably of obtaining different thicknesses of the sample film, the original absolute binding energy values of each peak is of no exact physical meaning and the correction was performed.

4. Contact angle measurements: Two kinds of methods, sessile drop and captive bubble (underwater),\cite{16} were carried out. The sessile dropping method was used to detect the surfaces within 15 s after the water droplet contacted the polymer. The water droplets were positioned with a syringe and the method of captive bubble was performed directly after 24 h of water equilibration of the samples. The air droplets were introduced through a syringe with a U-shaped needle into the double-distilled deionized water system. A JY-82 goniometer was used. All the droplets were no larger than $0.5 \mu L$. The dimensions of them, the width D and the height H, were measured from the scale on the lens of the microscope.

In vitro testing of static blood-compatibility

Approximately 1.5 ml mixed solution of PEL and MSPEO was vertically dropped into the $10 \times 100 \text{ mm}$ test tube. After
10 min the mixture was carefully taken out and the test tube was dried in vacuum for 15 min. The process was then repeated two more times after which the blended layer was coated on the inner surface of the test tube. The samples of glass, PEU control, PEU-MSPEO 2300, 6000 and 12000, were tested.

PRT: The human plasma in which the Ca²⁺ was removed (blood type: B, Central Blood Bank of Hangzhou) and the solution of CaCl₂, 0.025 mol/L were warmed up to 37°C. 0.1 ml of plasma was placed into the treated test tube, and 60 s later the CaCl₂ solution added. This recalcified plasma was then stirred with a small stainless steel hook and the process was timed until the silky fibrin appeared. The data of PRT were recorded and the process was repeated six times to obtain an average value.

Results and discussion

Characterization of synthesized products

The route of the SPEO and MSPEO’s synthesis is as follows, as given by the ¹H NMR data (Fig. 2a and b):

\[
\text{CH}_3(\text{CH}_2)_{17}\text{OH} + \text{Na} \rightarrow \text{CH}_3(\text{CH}_2)_{17}\text{ONa} + \text{[EO]} \rightarrow \text{CH}_3(\text{CH}_2)_{17}\text{-PEO-OH;}
\]

SPEO: C_{18}-PEO-OH

2SPEO + MDI → SPEO-MDI-SPEO; MSPEO: C_{18}-PEO-MDI-PEO-C_{18}

Based on the anionic mechanism of the polymerization, the ideal \( M_n \) could be calculated by the formula: \( M_n = n [M]/[C] \). Where \([M]\) is the mass-concentration of the monomer, \([C]\) the molar-concentration of the initiator and \( n \) the number of initiator molecules per polymer chain, in this case \( n = 1 \). The practical value of \( M_n \) was calculated according to the integral value of the ¹H NMR peak area with the certain intrinsic standard, i.e. the peak area of stearyl end groups at \( \delta = 1.3 \) ppm. The formula used is:

\[
M_n = 44 \cdot \left( \frac{A_{\delta=1.6}}{A_{\delta=1.3}/(2 \times 15)} \right) + M_{\text{stearyl}}
\]

where \( A \) is the integral value of the peak area; \( 2 \times 15 \) the approximation of the methylene proton number per molecule of stearyl group corresponding to the peak at \( \delta = 1.3 \) ppm. The value deduced from the formula within the parentheses is the number of EO groups per chain of PEO corresponding to the peak at \( \delta = 3.6 \) ppm, and 44 is the molecular weight of EO group, \( M_{\text{stearyl}} \) is the molecular weight of the stearyl group. Thus, the number of methylene groups per molecule of stearyl group corresponding to the peak at \( \delta = 1.3 \) ppm, \( n = 15 \), is deduced from the equation

\[
A_{\delta=1.3}/2n = A_{\delta=0.9}/3
\]

where the peak corresponding to the methyl end group of the stearyl group is at \( \delta = 0.9 \) ppm. Both the ideal values and the experimental values of each sample were listed in Tab. 1.

Surface analysis

1. ATR-FTIR: The ATR-FTIR data for the samples are shown in Fig. 3. The H-bonded \( \text{--NH--} \) bands are found at 3340 cm⁻¹, \( \text{--CH--} \) bands are found at 2960–2850 cm⁻¹, the non-H-bonded urethane carbonyl \( \text{--CO--} \) and H-bonded \( \text{--CO--} \) bands are at 1730 cm⁻¹ and 1703 cm⁻¹, and ether \( \text{--O--} \) bands at 1110 cm⁻¹. In this paper the various-sized MSPEOs were blended into the matrix PEU. The behavior of the different MSPEOs’ surface enrichment, i.e. the effect of the SMA’s different size to the blending samples’ surface structure will be studied. From the ten samples (PEL control; PEL-MSPEO 1700, 2300, 6000 and 12000, on air and water interface respectively), two ratios, \( \text{--O--/--CH--} \) (1110 cm⁻¹/2850 cm⁻¹) and \( \text{--O--/--CO--} \) (1110 cm⁻¹/1703 cm⁻¹), were reported (shown in Fig. 4a and 4b respectively). The data of PEL-MSPEO 1700 was according to that we
Fig. 3. Raw data of ATR-FTIR spectra: from the bottom to the top, PEL control, PEL-MSPEO 12000, 6000 and 2300, in air (A) and on the water interface (B) respectively.
Various-sized stearyl poly(ethylene oxide) coupling-polymer blending poly(ether urethane) ...

reported previously.\textsuperscript{11} Since the ratio of $\mathrm{O}^/-/\mathrm{CH}_2^-$ on the soft blocks of PEU, poly(tetramethylene glycol) (PTMG) is 1/4, while in MSPEO on the chain of SPEO it is approximately 1/2, thereby the increase of this ratio indicates PEO chains’ surface enrichment. Fig. 4b represents the complementary references.

Fig. 4a and 4b indicate that PEO chains were largely enriched on the air interface of PEL-MSPEO 1700 and 2300. But along with the chain of MSPEO increasing in length, the PEO-enrichment became weaker. With respect to PEL-MSPEO 12000 there was almost no enrichment of PEO. We know that the main drive of this enrichment on the air interface comes from the C\textsubscript{18} end groups. The C\textsubscript{18} has rather poor compatibility with the matrix PEU and they have rather low surface energy on the air interface, therefore in air they will move to the top of the surface, and thus the PEO chain will also move towards the surface,\textsuperscript{11} as seen in Scheme 1b. The cases described above indicate that when the PEO chain is so short as that of MSPEO 1700 and 2300, the effect of C\textsubscript{18} will be particularly dramatic and the behavior of the whole molecule will mainly embody C\textsubscript{18}’s property. Since the whole molecule of small sized MSPEO with short-chain PEO is more moveable, its PEO and C\textsubscript{18} will be enriched on the air interface of PEL-(small)MSPEO more easily. However, for MSPEO 12000, C\textsubscript{18} is relatively small and not so powerful to drive the whole molecule, and the high surface energy of the larger PEO on the air interface it will counteract the surface enrichment. Therefore, the surface enrichment of long-chained MSPEO on the air interface is kinetically and thermodynamically hindered.

On the water interface Fig. 4a indicates that both for PEL-(small)MSPEO such as PEL-MSPEO 2300 and PEL-MSPEO(long-chained) such as PEL-MSPEO 12000, there was obvious enrichment of PEO. When compared to the corresponding cases on the air interface, Fig. 4b shows that for PEL-(small)MSPEO the enrichment was weakened, while the PEO chains enriched on

<table>
<thead>
<tr>
<th>( \delta/\text{ppm} )</th>
<th>Peak assignment</th>
<th>Integral peak area</th>
</tr>
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<tbody>
<tr>
<td>~0.86</td>
<td>$-\text{CH}_3$</td>
<td>c = 0.10</td>
</tr>
<tr>
<td>~1.25</td>
<td>R$-\text{CH}_2^-\text{R}'$</td>
<td>b = 1.00</td>
</tr>
<tr>
<td>~3.52</td>
<td>$-O\text{-CH}_2\text{-CH}_2^-O$</td>
<td>a = 6.44</td>
</tr>
</tbody>
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Tab. 1. \(^1\text{H} \text{NMR data for } M_n \text{ calculation of the SPEOs and naming of corresponding SPEOs, MSPEOs, PEL-MSPEOs.}

<table>
<thead>
<tr>
<th>Practical ( M_n )</th>
<th>2382</th>
<th>6055</th>
<th>12252</th>
</tr>
</thead>
<tbody>
<tr>
<td>E0(g)/Initiator in mol</td>
<td>45/0.015</td>
<td>80/0.01</td>
<td>150/0.01</td>
</tr>
<tr>
<td>Ideal ( M_n )</td>
<td>3000</td>
<td>8000</td>
<td>15000</td>
</tr>
</tbody>
</table>

Naming of Corresponding MSPEO & PEU-MSPEO

<table>
<thead>
<tr>
<th></th>
<th>MSPEO 2300</th>
<th>MSPEO 6000</th>
<th>MSPEO 12000</th>
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<tbody>
<tr>
<td>PEL-MSPEO 2300</td>
<td>PEL-MSPEO 6000</td>
<td>PEL-MSPEO 12000</td>
<td></td>
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Fig. 4. ATR-FTIR data ratios: (A) the ether groups, $-\text{O}^-$, and the methylene groups, $-\text{CH}_2^-$; (B) the ether groups $-\text{O}^-$ and the carbonyl groups, $-\mathrm{CO}^-$.

The samples are PEL control and PEL-MSPEO 1700, 2300, 6000, 12000, respectively on the air interface and water interface.

PEL-MSPEO(long-chained) greatly increases. The explanation is that on the water interface, the result of the competition between the hydrophilic PEO chain and the
Fig. 5. Raw and curve-fit data of the C1s XPS collected at 0° take-off angle: (A) PEL control; (B), (D) and (F), respectively, PEL-MSPEO 2300, 6000 and 12000 on air interface; (C), (E) and (G), respectively, PEL-MSPEO 2300, 6000 and 12000 on water interface. The component peaks are O–C–C at 285.3 eV, O–C–O at 286.8 ev and O=C–O at 289.5 eV, respectively.
hydrophobic C$_{18}$ will dominate the final behavior of whole MSPEO molecule. The hydrophilic PEO chain will stretch out and the hydrophobic C$_{18}$ will bend down back to the bulk. For MSPEO 12000, the long PEO chain is the leading factor for the behavior of the whole molecule. Given sufficient water leaching, the long chain of PEO will finally be enriched at the surface in spite of the negative effect of C$_{18}$. However, for the short-chained MSPEO, the bending back of C$_{18}$ will quickly lead to a lessening of the PEO’s enrichment and the surface conformation turning into the hydrophobic “loop” structure (Scheme 1c). Although the PEO enrichment was weakened at the surface of PEL-MSPEO 2300, the MSPEO2300 with loop-conformation was still largely present at the interface.

2. XPS: Since the 400 nm depth$^{[18]}$ of penetration of the ATR-FTIR radiation penetrates deeply and thereby not very surface sensitive, the characterization of angle-dependant XPS was carried out. High-resolution spectra were obtained for C1s electrons at varying TOA (θ) ranging from 0, 30, 60 to 90°. The depth (D) detected by XPS in the polymer samples is according to $D = \frac{3\lambda}{\cos\theta}$, where the $\lambda$ is the mean free path. Therefore, electrons emanating from the assumed maximum depth $D$ of approximately 10 nm (100% 3\lambda) can be detected with TOA 0°. Consequently, as the TOA is increased, the depth $D$ decreases; the TOA 30, 60 and 90° represent an assumed approximate sampling depth of 8 nm (to 86%), 5 nm (to 50%) and <1 nm, respectively (to <10% of the maximum sampling depth).

The spectra with TOA 0° were selected to be analyzed according to three component peaks, as seen in Fig. 5. They were respectively O=C–C at 285.3 eV, O=C–O at 286.8 eV and O=C–O at 289.5 eV. The ratios of O=C–O/O=C–C and O=C–O/O=C–C were 285.5/285.3 and 286.8/285.3 respectively (Fig. 6a and b).

Obviously, the increase of O=C–O/O=C–C indicates the surface enrichment of PEO chains and this was observed to be similar both in air and water, as shown by ATR-FTIR. Thereby we can draw a conclusion that the information at a depth of 10 nm was approximately the same as the weighted mean result within 400 nm sampling depth of ATR-FTIR. In Fig. 6b, the urethane carbonyl’s increase, which represented the surface enrichment of M-blocks on MSPEO and/or “hard” blocks of PEU, was synchronous with that of PEO. This indicates that the enrichment is the behavior of the whole molecule of MSPEO, and it draws the H-bond linked PEU chain together.

As seen in Fig. 7, the samples of PEL-MSPEO 2300 and 12000, on air and water interfaces respectively, were characterized by various TOA of 0, 30, 60 and 90°. Besides the three component peaks listed above, the forth peak of C–C–C on C$_{18}$ at 284 eV was observed. According to the various TOAs, the ratios of C–C–C/C 1 s (284/284 ~ 290) at the corresponding sampling depth are shown in Fig. 8. They were used to study the C$_{18}$ content at the different depths of the surface layer for each sample in air and water. Consequently, the more detailed representation of the MSPEOs’ behavior was expected. Whether in air or water, for the long-chained MSPEO12000, within the surface layer of 10 nm’s thick the relative distribution of C$_{18}$ content was the same and the C$_{18}$ was evenly distributed in the depth of 0 ~ 8 nm. Nevertheless the absolute quantity of C$_{18}$ on the water interface was much larger than that in air. This indicates that the hydrophilic PEO chain’s enrichment on the water interface managed to escape from the hydrophobic C$_{18}$ and thus they were also enriched at the interface. While in air the spontaneous surface enrichment of C$_{18}$ was also kinetically restrained by the large size of the PEO chain. Therefore, for the monoblock behavior of long-chained MSPEO the dominant factor is undoubtedly the hydrophili-
lic PEO chain. However, for the short-chained MSPEO2300, when at the air interface the C18 is enriched within 4 nm’s of the surface, mainly at <2 nm. On the water interface, considerable hydrophobic C18 chains bent back to the level of 4–10 nm. This shows that for the behavior of short-chained MSPEO, the movement of C18 can not be dominated by the PEO chain and the fact on the contrary is true.

3. Contact angle measurements: Two methods of contact angle measurements, the sessile drop and captive bubble, were performed. According to the measured dimensions, width D and height H, the formula for the method of sessile drop is \( \theta = 2 \tan^{-1}(2H/D) \), \( \theta < 90^\circ \), and for the method of captive bubble is \( \theta = \cos^{-1}(2H/D-1) \), \( \theta < 90^\circ \). The results are shown in Fig. 9. According to the sessile drop method, the contact angle decreased from PEL control’s 36° to PEL-MSPEO 2300’s 12.3°, but along with the size of MSPEO increasing, the angle obviously increased. However, the results from the captive bubble method indicated that the contact angle of all the PEL-MSPEOs decreased more compared to those of the PEL control.

The data from the sessile drop method indicate the advancing contact angle 15 s after the water droplet contacts the original air interface of the samples. The data from the captive bubble method are fairly close to the equilibrated receding water contact angle. Therefore, having been sufficiently equilibrated in water, as is car-
ried out in the captive bubble method, the hydrophilicity of each treated sample was effectively increased due to the full surface enrichment of the PEO chains. However, from the result of sessile drop method, within a very short time the long-chained MSPEO12000 could not be effectively enriched on the water interface. Within the same short period, the originally enriched short-chained MSPEO 2300 could accomplish the conversion from the hydrophobic conformation on air interface to “loop’s” hydrophilic conformation in water (Scheme 1c).

In vitro testing of static blood-compatibility

PRT: The in vitro testing of plasma recalcification time, PRT, was carried out (Fig. 10). The average values given out were calculated from six sets of data of each sample. The results indicate that after the Ca\textsuperscript{2+} (Factor IV) was added to the anti-coagulated human plasma, and on immediate contact with the samples, the intrinsic blood-coagulation system was initiated and prothrombin (Factor II) began to be converted into thrombin. However, compared to the cases of glass and PEL control, the PRT was obviously prolonged at the surface of the PEL-MSPEOs. The reason why the anti-coagulation effect of PEL-MSPEO 12000 was relatively weak might possibly lie in the short contact time between the sample and the aqueous plasma. As explained above, on contact with water, the short-chained MSPEO can turn itself into the hydrophilic loop-conformation quickly and from the very beginning to the end there is always considerable PEO enrichment at the interface. However, for long-chained MSPEO 12000 and without the enough pre-treatment of water leaching, within 3 ~ 4 min the PEO chain’s surface enrichment can not be accomplished.

Conclusions

The stearyl poly(ethylene oxide) (SPEO) with various values of $M_n$, i.e. 2300, 6000 and 12000, was polymerized. Consequently the amphiphilic coupling polymers of 4,4’-diphenylmethane disocyanate (MDI)-SPEO (SPEO-MDI-SPEO, MSPEO 2300, 6000 and 12000) were synthesized and the blended poly(ether urethane) samples of PEL-MSPEOs (PEL-MSPEO 2300, 6000 and 12000) were prepared through a solution process.

The surface analysis through ATR-FTIR, angle-dependent XPS and two methods of contact angle measurements were performed and the conclusion is as follows. For the MSPEO molecule, C\textsubscript{18} has rather a poor compatibility with the PEL matrix and has rather a low surface energy on the air interface, which makes its main drive of MSPEOs’ surface enrichment in air. C\textsubscript{18} is, in addition, hydrophobic which restrains enrichment at the water interface. Also, the PEO chain can not be very
compatible with the PEL soft block, yet the surface energy of it on the air interface is high and as it is hydrophilic, which makes it the drive of MSPEOs’ surface enrichment on water interface, there is a resistance for the enrichment in air. Given the various sizes of PEO, the behavior of MSPEO was different. In air, towed by $C_{18}$, the small-sized MSPEO 2300 could quickly accomplish the surface enrichment through monoblock movement and formed an interface with the lowest energy. However, for long-chained MSPEO 12000 the same procedure was hindered by the large size of the PEO and the small SMA managed to be present in surface layer. Nevertheless, when the environment was changed to aqueous, the SMA’s enrichment could be achieved at the surface of both PEL-MSPEO 2300 and 12000. However, the mechanism was different. As a result of the competition between the hydrophilic PEO and the hydrophobic $C_{18}$, with a relatively long duration of monoblock movement, the large-sized SMA was dramatically and steadily enriched at the PEL-MSPEO 12000 interface. However, for MSPEO 2300, within a short time the hydrophilic “loop” structure developed (Scheme 1c). Although due to the $C_{18}$’s effect the original surface enrichment was weakened, there was still considerable and sufficient SMA at the interface. In other words, the dominant factor for the monoblock behavior of long-chained MSPEO 12000 is the PEO chain, while for PEL-MSPEO 2300 interface the key factor is $C_{18}$. But the fact that on the water interface there is a considerable enrichment of both $C_{18}$ and PEO chains shows that the dominant effect of $C_{18}$ for short-chained MSPEO is not so overwhelming as that of PEO for long-chained MSPEO. At the same time, the molecular size will also dramatically affect MSPEOs’ kinetic behavior including the monoblock mobility during the enrichment from the bulk to the surface and the reconstructing of surface conformation in different environments. Undoubtedly, the smaller the size the faster the movement.

Part of above can also be confirmed by the results of an anti-coagulation experiment, PRT, in which the blood compatibility of the PEL-MSPEOs had been improved considerably compared to that of the PEL control.

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