# Comparison of surface segregation and anticoagulant property in block copolymer blended evaporation and phase inversion membranes

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In our recent study, an ABA amphiphilic triblock copolymer poly(vinyl pyrrolidone)-b-poly(methyl methacrylate)-b-poly(vinyl pyrrolidone) (PVP-b-PMMA-b-PVP) was synthesized and directly blended with polyethersulfone (PES) to prepare membranes. To further investigate the effects of surface energy and miscibility on the near-surface composition profile of the membranes, evaporation membrane and phase inversion membrane of PES/PVP-b-PMMA-b-PVP were prepared by evaporating the solvent in a vacuum oven, and by a liquid–liquid phase separation technique, respectively. The surface composition and morphology of the membranes were investigated using XPS and tapping mode atomic force microscopy, and the surface segregations of the membranes were compared and discussed. For the evaporation membrane, PVP blocks were buried below the lower surface energy PMMA blocks and PES substrate at the airside surface. For the phase inversion membrane, however, the hydrophilicity of PVP blocks were the biggest driving force because of the high speed exchange between water and solvent, and present at the membrane surface. Thus, the modified PES membrane prepared by using phase inversion method has a layer of PVP block brushes on its surface and has the better anticoagulant property, which might improve the blood compatibility of the membrane and has potential to be used in blood purification. Copyright © 2012 John Wiley & Sons, Ltd.

**Keywords:** surface segregation; evaporation membrane; phase inversion membrane; amphiphilic triblock copolymer; polyethersulfone membrane

## Introduction

It is well known that polymeric materials are widely used in blood purification fields for artificial organs, medical devices, and disposable clinical instruments, such as hemodialysis, hemofiltration, plasmapheresis, and plasma collection.[1,2] Polyethersulfone (PES) is one of the most widely used polymeric materials. PES and PES-based membranes show outstanding oxidative, thermal, and hydrolytic stability and good mechanical and film-forming properties.[3–6] To improve the blood compatibility of the membranes, many studies have focused on the modification of the materials, including blending, coating, surface physical treatment, surface grafting, etc.[7–9] Among the modification methods, blending is the simplest method and is widely used in the industry.

In our recent study, an ABA amphiphilic triblock copolymer poly(vinyl pyrrolidone)-b-poly(methyl methacrylate)-b-poly(vinyl pyrrolidone) (PVP-b-PMMA-b-PVP) was synthesized by RAFT polymerization.[10] The block copolymer can be directly blended with PES using dimethylacetamide (DMAC) as solvent to prepare flat-sheet and hollow fiber membranes by using a liquid–liquid phase separation technique. The modified membranes showed lower protein (bovine serum albumin) adsorption, suppressed platelet adhesion, and prolonged blood coagulation time, and thereby improve the blood compatibility. It was also found that a PVP block brush was formed on the membrane surface.

To further understand how the block copolymer distributes inside the PES membrane and why the brush structure forms during the phase separation, in the present paper, we will discuss the effects of the surface energy and miscibility on the near-surface composition profile of the membranes, and the role of water in restructuring the surface in detail. The quantitative depth profiles for phase inversion and evaporation membranes were investigated.

## Materials and methods

### Materials

Polyethersulfone (Ultrason E6020P) was obtained from BASF, Germany. Methyl methacrylate (99.0%) was purchased from UNI-CHEM, China.

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*N*-Vinyl pyrrolidone (VP; 99.0%) and tetrabutylammonium hydrogen sulfate were purchased from Alfa Aesar, USA; VP was pretreated by activated carbons before use. *N*, *N*-Dimethylacetamide (DMAC, 99.0%) and *N*, *N*-dimethylformamide (DMF; 99.0%) were purchased from Chengdu Kelong Inc. (Chengdu, China) and used as the solvents. Azo-bis-isobutryonitrile was purchased from Chengdu Kelong Inc. (Chengdu, China), and 4,4′-Azobis(4-cyanovaleric acid) was purchased from Alfa Aesar China Co., Ltd. (Tianjin, China), both of which were used as the initiator.

### Synthesis of poly(vinyl pyrrolidone)-*b*-poly(methyl methacrylate)-*b*-poly(vinyl pyrrolidone)

*S,S′*-Bis(α,α′-dimethyl-α″-acetic acid)-trithiocarbonate was prepared according to a literature procedure.[11] Macro-RAFT agent of PVP and block copolymer of PVP-*b*-PMMA-*b*-PVP were synthesized by following a previously reported method.[10] For a typical preparation process, monomer (VP or methyl methacrylate), RAFT agent (*S,S′*-bis(α,α′-dimethyl-α″-acetic acid)-trithiocarbonate or carboxyl-terminated PVP), initiator (4,4′-azobis(4-cyanovaleric acid) or azo-bis-isobutryonitrile), and solvent (DMF) were added into a tube; after bubbling for 30 min with nitrogen, the reaction mixture was allowed to warm under a nitrogen atmosphere to 80 °C, and the polymerization was carried out for 5 h. After precipitating in ethyl ether, the product was dried under vacuum at 50 °C overnight. The obtained product was ground into fine powders and immersed into $H_2O$ and THF for one week respectively, and then the procedure was repeated for three times alternately, and finally dried in a vacuum oven at room temperature for 24 h.

### Preparation of evaporation membranes

Evaporation membranes used in this study were prepared by evaporating the solvent in a vacuum oven.[12] To prepare the membrane, polymers were dissolved in DMF to obtain a polymer solution, which was cast on a glass plate and spread with a uniform thickness, then dried in a vacuum oven at 40 °C for 3 days. The concentrations of PES and additive were 16% and 5% (wt%), respectively. The membrane was carefully washed with distilled water and dried at room temperature.

### Preparation of phase inversion membranes

The membrane of PES/copolymer was also prepared by liquid–liquid phase separation technique,[13,14] and termed phase inversion membrane. PES and the synthesized copolymer were dissolved in the solvent DMAC by vigorous stirring until a clear homogeneous solution was obtained. The concentrations of PES and additive were 16% and 5% (wt%), respectively. After vacuum degassing, the casting solution was prepared into membrane by spin coating coupled with a liquid–liquid phase separation technique at room temperature. The membranes were rinsed with distilled water thoroughly and dried at room temperature to remove the residual solvent.

### Characterization of the prepared membranes

The structures and the elements of the membrane surfaces were investigated by reflected fourier transform infrared (FTIR) Nicolet 560 (Thermo Fisher Scientific Inc., Madison, Wisconsin, America) and XPS. Atomic force microscopy studies were conducted using CSPM400 (Benyuan Nano-Instruments Ldt., China).

### Contact angles

The contact angles of the membrane surfaces were characterized on the basis of contact angle measurement using a contact angle goniometer (OCA20, Dataphysics, Germany) equipped with video capture. A piece of 2 cm × 2 cm membrane was attached on a glass slide and mounted on the goniometer. For the static contact angle measurements, a total of 3 μL interrogating liquids (diiodomethane was chosen as the nonpolar liquid, whereas water and ethylene glycol were chosen as the polar liquids) were dropped on the airside surface of the membrane at room temperature, and the contact angles were measured after 10 s. At least eight measurements were averaged to get a reliable value. The measurement error was ± 3°.

### Clotting time

To evaluate the antithrombogenicity of the modified membranes, the activated partial thromboplastin time (APTT) was measured by an automated blood coagulation analyzer CA-50 (Sysmex Corporation, Kobe, Japan), and the test method was described as follows: at the beginning of the APTT test, healthy human fresh blood (Dr. Fen R., healthy, man, Chinese, 32 years old) was collected in vacuum tubes containing sodium citrate as an anticoagulant (anticoagulant to blood ratio, 1 : 9 v/v), and the platelet-poor plasma (PPP) was obtained after centrifuging at 4000 rpm for 15 min. Synchronously, the membrane (0.5 cm 0.5 cm, three pieces) was immersed in 0.2 mL phosphate buffered saline (PBS) solution (pH = 7.4) for 1 h. The PBS solution was removed and then 0.1 mL of fresh PPP was introduced. After incubating at 37 °C for 30 min, 50 μL of the incubated PPP was added into a test cup, followed by the addition of 50 μL APTT agent (Dade Actin Activated Cephaloplastin Reagent from SIEMENS) (incubated 10 min before use), and incubated at 37 °C for 3 min. Thereafter, 50 μL of 0.025 M $CaCl_2$ solution was added, and then the APTT was measured. At least three measurements were averaged to get a reliable value, and the results were analyzed by statistical method.

## Results and discussion

The Hansen solubility parameter exerted incomparable influence on the understanding and prediction of the phase behavior of polymer blends. The Hansen solubility parameter refers to the density of cohesive energy,[15] which consists of three components: $\delta_h$, the contribution of the hydrogen bonding interaction; $\delta_p$, the contribution of the polar interaction; and $\delta_d$, the contribution of the dispersion interaction. In this study, the binary matrix composed of PMMA block and PES, which is based on the close principle of solubility parameters (see Table 1), can obtain good

**Table 1.** Solubility parameters of various polymers and DMAC[16]

| Name | $\delta_d$ (MPa$^{0.5}$) | $\delta_p$ (MPa$^{0.5}$) | $\delta_h$ (MPa$^{0.5}$) | $\delta_t$ (MPa$^{0.5}$) |
|------|------|------|------|------|
| PMMA | 18.6 | 10.5 | 7.5 | 22.7 |
| DMAC | 16.8 | 11.4 | 10.2 | 22.7 |
| PES | 17.6 | 10.4 | 7.80 | 21.9 |

$\delta_t$, total solubility parameter, which is defined as: $\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$, $\delta_d$ dispersive contribution, $\delta_p$ polar contribution, $\delta_h$ hydrogen bonding contribution.

dispersion effect.[16] PVP could be directly blended with PES to prepare membranes and the adoption of PVP as the hydrophilic block for membrane could provide a miscible polymer blend system during membrane formation because of the strong donor/acceptor interaction between O=C–N functional groups from PVP block and O=S=O and/or benzene ring from PES polymer.[17,18] These results indicate that the blend system of PVP-*b*-PMMA-*b*-PVP/PES is a compatible system, which has been confirmed by the fact that the polymer solution appears transparent in DMAC (PES 16 wt%; PVP-*b*-PMMA-*b*-PVP 5 wt%).

The block copolymer can be directly blended with PES and formed a compatible system. However, the surface segregation of the membrane will be influenced by the relative surface energies of the two blocks and PES substrate. Measurements of liquid–solid contact angles ($\theta$) are commonly used to evaluate solid surface tension, $\gamma_S$. However, the correlation between $\theta$ and $\gamma_S$ is still a controversial problem.[19] The surface energy of a polymer is always determined by measuring the static contact angle of water on the substrate and then calculating using Fowkes' equation (see Eqn (1)).[20] It is doubtful that the Fowkes' equation, in the stated form, can correctly measure the polar component of the surface energy. For the surfaces of highly polar polymers (low water contact angles), the van Oss–Chaudhury–Good method (see Eqn (4), which leads to a Young's Eqn (5)), or the Owens–Wendt (see Eqn (2) combined with the Young's equation yields (3)) method is usually used.[21]

$$\gamma_S = \gamma_L(1 + \cos\theta)^2/4 \quad (1)$$

$$\gamma_S = \gamma_S^d + \gamma_S^p \quad (2)$$

$$\gamma_L(1 + \cos\theta) = 2\left[(\gamma_S^d\gamma_L^d)^{1/2} + (\gamma_S^p\gamma_L^p)^{1/2}\right] \quad (3)$$

$$\gamma_S = \gamma_S^{LW} + 2(\gamma_S^+\gamma_S^-)^{1/2} \quad (4)$$

$$\gamma_L(1 + \cos\theta) = 2\left[(\gamma_S^{LW}\gamma_L^{LW})^{1/2} + (\gamma_S^+\gamma_L^-)^{1/2} + (\gamma_S^-\gamma_L^+)^{1/2}\right] \quad (5)$$

where $\gamma^d$ and $\gamma^p$ are the dispersion and the polar components, respectively, of the solid, $\gamma_S$, and liquid, $\gamma_L$, surface tensions; $\gamma_S^{LW}$ is the Lifshitz–van der Waals dispersive component; $\gamma_L^-$ is the polar electron-donor (Lewis base) component; and $\gamma_L^+$ is the polar electron-acceptor (Lewis acid) component.

Poly(vinyl pyrrolidone) and PVP-based copolymer are highly polar (low water contact angles) materials. The surface energies of PVP, PMMA, and PES were determined by measuring the static contact angles with water, diiodomethane, and ethylene glycol on the substrate and then calculating using the surface tension component of van Oss, Chaudury, and Good (vOCG), which rely on the Fowkes' model that assumes the total surface energy is the sum of different interaction components (van der Waals dispersive, dipole, hydrogen bonding, etc.) at the liquid–solid interface and postulates a geometric mean relationship for both of the solid–liquid and liquid–liquid interfacial tensions.[22–24] To evaluate the surface energies of PVP, PMMA, and PES, and compare the surface segregation in the membranes, the evaporation membrane was first prepared and investigated.

The van Oss–Chaudhury–Good approach involves three different surface tension components, and at least three different liquids (two polar and one nonpolar) are needed for the three equations that can be solved for the unknowns $\gamma_S^{LW}$, $\gamma_S^-$, and $\gamma_S^+$.

Thus, the dispersion contribution $\gamma^d$ corresponds to $\gamma^{LW}$, whereas the polar contribution of $\gamma^d$ is further split into the Lewis acid and base components $\gamma^{\pm}$ [21]. Here, diiodomethane was chosen as the nonpolar liquid, whereas water and ethylene glycol were chosen as the polar liquids. Static contact angles of PVP, PMMA, and PES were measured using water, diiodomethane and ethylene glycol, respectively. The polymer surface energies calculated according to the van Oss–Chaudhury–Good approach are summarized in Table 2.

As shown in Table 2, PMMA and PES have similar values of surface energy, which are lower than that of PVP. Generally, polymers with higher surface energy are usually buried below lower surface energy polymers.[25–28] Thus, it is deduced that for the evaporation membrane, PVP blocks were buried below PMMA blocks and PES substrate, and dispersed in the PES matrix, which will be further confirmed by angle-resolved XPS analysis.

Table 3 presents the angle-resolved XPS data of the membrane surface for PES/PVP-*b*-PMMA-*b*-PVP evaporation membrane. The S concentration (atom %) decreases and N concentration increases with an increase in the XPS probe depth. The element contents of N for the blended membrane surface were 5.29% (mole ratio, depth: 9 Å), which was close to the N original contents of the PVP (the degree of PVP surface coverage was calculated to be 30.98%). These results indicate that for the block copolymer PVP-*b*-PMMA-*b*-PVP blended membranes, large amounts of PVP blocks were buried below the PMMA blocks and PES substrate at the air side, and only small amounts of PVP blocks on the surface of the PVP-*b*-PMMA-*b*-PVP blended evaporation membrane (see Fig. 1).

However, to improve the biocompatibility of the PES membranes, the hydrophilic block (PVP) should be present at the surface of the membrane (and surface of the membrane pores). Special approaches are generally required to drag a high surface energy block to the surface of a coating,[29] and in this paper, liquid–liquid phase separation method was used.[30,31] During the phase separation, the hydrophilicity was the biggest driving force for the migration and self-assembly of the block copolymer. Phase separation occurs at the interface between

**Table 2.** Static contact angles and surface energies of the polymers[a]

| Polymer | $\theta_w$ (°) | $\theta_{DI}$ (°) | $\theta_{EG}$ (°) | $\gamma_S^{VOCG}$ [b] |
|---------|---------|---------|---------|---------|
| PVP | 37.1 | 16.1 | 51.0 | 48.832 |
| PMMA | 71.5 | 31.0 | 48.2 | 43.894 |
| PES | 74.3 | — | — | 46.0[c] |

[a]Evaporation membrane.
[b]Calculated with the van Oss–Chaudhury–Good method.
[c]According to the literature value.

**Table 3.** Angle-resolved XPS results for the evaporation membrane surfaces

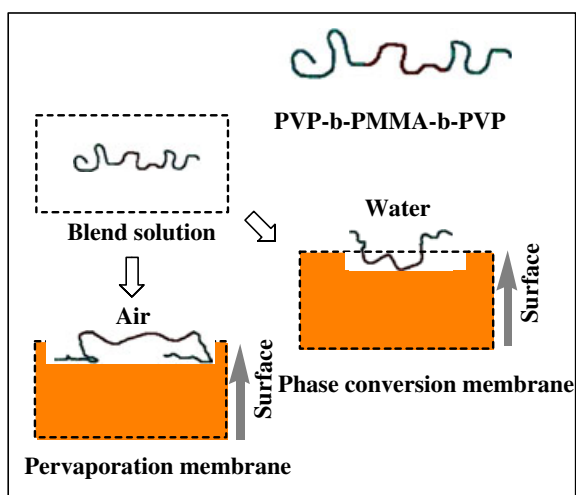| Depth ($\lambda$) | C (%) | O (%) | N (%) | S (%) |
|---------|-------|-------|-------|-------|
| 9 Å | 71.08 | 25.74 | 1.01 | 2.25 |
| 57 Å | 62.55 | 34.11 | 2.75 | 0.58 |
| 80 Å | 61.78 | 35.00 | 2.70 | 0.52 |

**Figure 1.** Illustrations of the formation mechanism for evaporation membrane and phase inversion membrane.

PES and water in seconds, which may be the underlying reason for the orientation of the block copolymer with the PVP block being present at the surface and the PMMA block being embedded in the substrate (see Fig. 1). There may be abundant copolymer concentrated on the surface of the membrane and a layer of PVP brush formed, which can be further confirmed by FTIR and XPS analysis.

Figure 2 shows a comparison on the FTIR spectra of the outer and inner parts of the modified PES membrane prepared by using phase inversion separation method. In the spectra of the membranes, the absorption peaks of carbonyl of PVP and PMMA at 1734.8 and 1668.2 cm$^{-1}$ were characterized, respectively. Compared with the peaks at 1733.8 and 1668.2 cm$^{-1}$ for the two sides of the modified membrane, it was observed that the two peaks of the outer side were stronger than that of the inner side, which indicated that there were abundant block copolymers on the outer surface (water side) compared with that on the inner part of the membrane (glass side).

The angle-resolved XPS experiment shows that the S content increased and the N content decreased obviously as the depth of the incident X-ray intensified, as shown in Table 4. Examination of the surface by contact angle and XPS revealed that the PVP
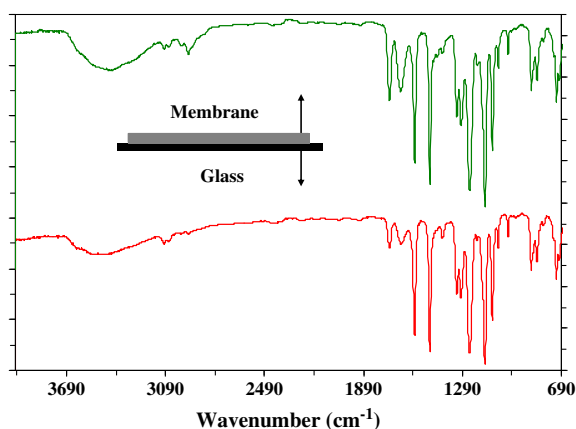
**Table 4.** Angle-resolved XPS results for the modified membrane surfaces (mole ratio) [10]

| Depth ($\lambda$) | C (%) | O (%) | N (%) | S (%) |
|---|---|---|---|---|
| 9 Å | 48.75 | 45.89 | 5.29 | 0.17 |
| 21 Å | 60.59 | 34.84 | 4.24 | 0.33 |
| 57 Å | 60.89 | 34.83 | 3.75 | 0.53 |
| 80 Å | 62.62 | 33.41 | 3.39 | 0.58 |

blocks migrate to the surface of the membrane and there is compositional gradient near the surface of the membrane. The element contents of N for the blended membrane surface were 5.29% (mole ratio, depth: 9 Å), which was close to the N original contents of the PVP (the degree of PVP surface coverage was calculated to be 96.88%). Also, the surface energy of PVP-*b*-PMMA-*b*-PVP/PES membrane was 47.266 mJ/cm$^2$, which was calculated according to the van Oss–Chaudhury–Good approach using the static contact angle data of the blended membrane with water, diiodomethane, and ethylene glycol (see Fig. 3 and Table 5).

It was found that the surface of the modified membrane prepared using the phase inversion method was rough with lots of tiny grooves and fine holes, as shown in Fig. 4. In the formation processes of evaporation and phase inversion membranes, the driving force, and the time for migration and self-assembly of the macromolecules were different. For the evaporation membrane, solvent volatilization was the biggest driving force for the migration and self-assembly of the polymer and block copolymer. Also, the solvent volatilization was very slow and there was enough time for the migration and self-assembly of the polymer and block copolymer, therefore the surface of the evaporation membrane was relatively smooth. However, for
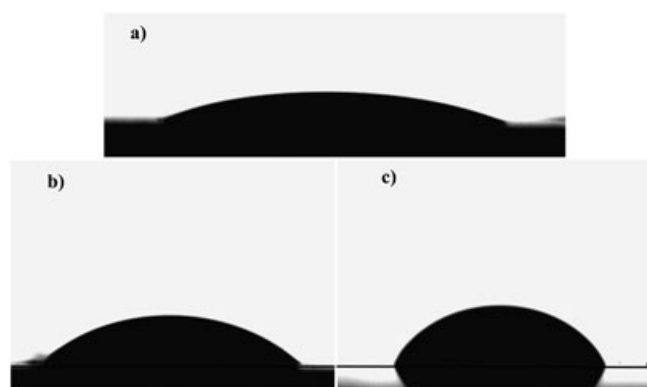


**Figure 3.** Static contact angles of the blended membrane with (a) diiodomethane, (b) ethylene glycol, and (c) water.



**Figure 2.** FTIR spectra for PVP-*b*-PMMA-*b*-PVP/PES membrane (prepared by phase inversion method) surfaces.

**Table 5.** Static contact angles and surface energy of the blend membrane[a]

| Membrane | $\theta_w$ (°) | $\theta_{DI}$ (°) | $\theta_{EG}$ (°) | $\gamma_S^{VOCG}$ [b] (mJ/m$^2$) |
|---|---|---|---|---|
| Blend membrane | 60.1 | 21.7 | 44.4 | 47.266 |

[a]Phase inversion membrane.
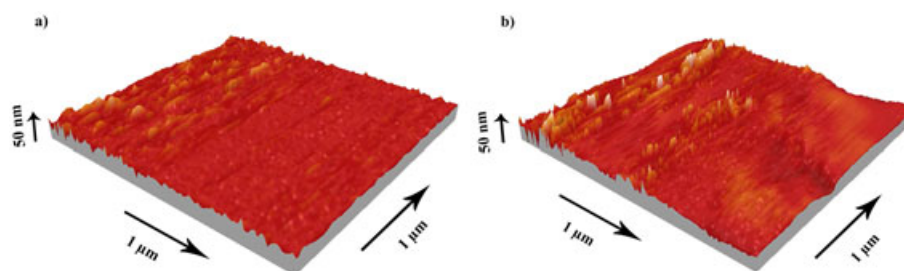[b]Calculated with the van Oss–Chaudhury–Good method.

**Figure 4.** Representative atomic force microscopy images of (a) evaporation membrane and (b) phase inversion membrane.
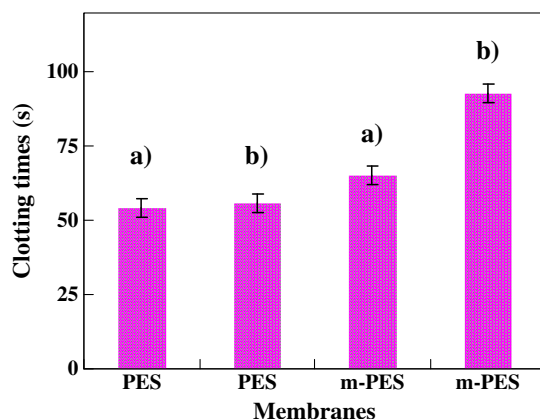


**Figure 5.** APTTs for PES and modified PES membranes prepared by (a) evaporation and (b) phase separation methods. $n = 3$.

phase inversion membrane, hydrophilicity was the biggest driving force for the migration and self-assembly of the polymer and block copolymer because of the high exchange speed between water and DMAC. Phase separation occurs at the interface between PES and water in seconds, and thus lots of tiny grooves and fine holes were left behind and a rough surface was obtained.

As mentioned above, different surface morphologies and different degrees of PVP surface coverage of the modified membranes were observed because of the different formation processes for evaporation and phase inversion membranes (the degrees of PVP surface coverage of evaporation and inversion membranes were calculated to be 30.98% and 96.88%). For the pure PES membranes, there was no significant difference in the anticoagulant property, as shown in Fig. 5 (the APTTs of PES prepared by evaporation and phase inversion membranes are 54.2 and 55.6 s, respectively). However, for the PVP-*b*-PMMA-*b*-PVP modified PES membranes, the APTT of the modified membrane prepared by phase inversion method increased compared with the modified membrane prepared by evaporation method, nearly an increase of about 42%. These results also indicate that there was more copolymer concentrated on the surface of the phase inversion membrane than that of the evaporation membrane. The modified PES membrane prepared by phase inversion method has the potential to be used in blood purification including hemodialysis and bioartificial liver support, and the study provided useful information for real application of phase inversion membranes.

## Conclusion

In summary, the amphiphilic triblock copolymer of PVP-*b*-PMMA-*b*-PVP can be directly blended with PES to form a miscible polymer blend because of the close solubility parameters and the strong donor/acceptor interaction of PVP block, PMMA block, and PES substrate, and can be prepared into evaporation and phase inversion membranes. The membrane surface segregation was usually influenced by the relative surface energy. For PES/PVP-*b*-PMMA-*b*-PVP evaporation membranes, PVP blocks were buried below the lower surface energy PMMA blocks and PES substrate. For PES/PVP-*b*-PMMA-*b*-PVP inversion membranes, however, hydrophilicity was the biggest driving force, and the PVP blocks were concentrated at the membrane surface. Thus, the modified PES membrane prepared by phase inversion method has a layer of PVP block brush on its surface and thus has the better anticoagulant property, which has the potential to be used in blood purification including hemodialysis and bioartificial liver support. The study provided useful information for the real application of the evaporation and phase inversion membranes.

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