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Supplementary information

Fabrication and performance study of zwitterionic polyimide antifouling ultrafiltration membrane

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Experimental

Monomer and polymer characterization

The sulfonated aromatic diamine monomer BAPBS was identified by elemental analysis, which was performed on an Elemental Analyses MOD-1106, such as C, H and N.

Fourier transform infrared spectroscopy (FTIR, Bruker Vertex 80V) was used to investigate the chemical structures of the BAPBS monomer, the zwitterionic and reference PI copolymer via the KBr pellet method. Absorbance spectra were obtained in the region of 4000-400 cm^{-1} with resolution 4 cm^{-1} for 32 scans. All the spectra were baseline corrected.

^{1}H NMR experiments were carried out on a Bruker 510 spectrometer (500 MHz for ^{1}H) using DMSO-d_6 as solvent. Tetramethyl silane (TMS) was used as an internal reference.

Thermal transitions of the zwitterionic and reference PI copolymers were studied by using a modulated DSC (Mettler DSC821e) instrument at a heating rate of 10 ºC/min under a nitrogen flow of 200 mL/min. The second heat was used to assess glass transition temperature (T_g).

The thermogravimetric analysis (TGA) was employed to assess the thermal stability of the copolymers with a Perkine Elmer Pyris 1 analyzer under nitrogen atmosphere (100 mL/min) at a heating rate of 10 ºC/min. Before analysis, the samples were dried and kept in the TGA furnace at 100 °C in a nitrogen atmosphere for 10 min, and then reheated to 800 °C at 10 ºC/min, and the temperatures at 5% and 10% weight loss were recorded for each sample.

The inherent viscosity measurements were carried out with an Ubbelohde viscometer at a concentration of 0.5 g/dL in DMF at 25 ± 0.1 ºC.

Results and discussion

Characterization of the sulfonated aromatic diamine monomer BAPBS

In this work, BAPBS was synthesized by two steps of reactions with an overall yield of 55.6%. The chemical structure of BAPBS was characterized by FTIR spectrum as displayed in Fig. S1. Two characteristic absorption peaks were clearly observed at 3417 and 3343 cm^{-1}, which could be attributed mainly to the N–H stretching vibration of amino group (–NH$_2$). The broad absorption bands around 1086 and 1028 cm^{-1} could be assigned to symmetric and asymmetric stretching of the sulfonic acid group (O=S=O). The strong adsorption peak at 1220 cm^{-1} only corresponds to Ar-O-Ar group was also observed in the spectrum of the BAPBS monomer. Meanwhile, the ^{1}H NMR spectrum of the BAPBS monomer is shown in Fig. S2. All spectral signals were assigned to the protons of the BAPBS structure. In addition, the elementary analysis result for BAPBS was in good agreement with the calculated one. These results clearly confirm that the diamine monomer prepared herein is consistent with the proposed structure.

^{1}H NMR (DMSO-d_6, ppm): 7.21 (d, 1H), 6.77 (dd, 1H), 6.70 (dd, 4H), 6.59 (d, 1H), 6.55 (dd, 4H), 4.87 (d, 4H).

Elem. Anal. Calcd for $C_{18}H_{15}KN_2O_5S$ (molecular weight: 410.49): C, 52.67%; H, 3.68%; N, 6.82%. Found: C, 52.48%; H, 3.79%; N, 6.77%.

Characterization of the zwitterionic and reference PI copolymers

The aromatic zwitterionic and reference PI random copolymers described herein were synthesized by a one-pot, high-temperature polycondensation method, and the ionic group concentration in the final membrane was accurately controlled by varying the molar ratio of different monomers. The molar percentages of the monomers for the copolymers preparation are listed in Table S1, and the viscosity characterization indicates that all obtained copolymers have high molecular weight.

To clearly understand, the chemical structures of the zwitterionic and reference PI copolymers were thoroughly characterized by FTIR spectroscopy. As shown in Fig. S3, the spectra displays the adsorption bands at 1776 and 1722 cm^{-1} corresponding to the symmetric and asymmetric vibration of imide carbonyl groups and do not show an amide carbonyl peak at 1650 cm^{-1}, thus indicating complete imidization during polycondensation. The absorption peak around 1379 cm^{-1} could be assigned to asymmetric stretching of C-N groups. These characteristic absorption peaks were almost consistent for both the zwitterionic PI copolymer and the reference PI copolymer. Compared to the FTIR spectrum of the reference PI, two new absorption peaks at 1078 and 1020 cm^{-1} were observed only for the zwitterionic PI which could be attributed to symmetric and asymmetric stretching of the sulfonic acid group (O=S=O). It could be indicated that the zwitterionic PI copolymer and the reference PI copolymer were successfully synthesized as expected. Moreover, the structure of the zwitterionic PI copolymer was identified by ^1H NMR spectrum, which is shown in Fig. S4. All signals were well assigned, and the expected copolymer structure was confirmed.

The glass transition temperatures (T_g) of the zwitterionic and reference PI random copolymers had been investigated with differential scanning calorimetry (DSC) under nitrogen, and the result is shown in Fig. S5. All the investigated copolymers are amorphous polymers, and the DSC results showed an increase of T_g in the presence of pendent sulfonic acid and tertiary amine groups. This phenomenon could be explained by the introduction of the ionic groups: firstly, increase the intermolecular interaction between molecular chains by pendant ions; and secondly, increase molecular bulkiness will result in difficulty in segment movement.

The thermal stability of the zwitterionic and reference PI copolymers had been investigated by thermogravimetric analysis (TGA) measurement under flowing nitrogen. Fig. S6 shows the typical TGA curves. There was only one weight loss step for the reference PI copolymer above 500 ºC, which was assigned to the degradation of the polymer chain. However, the zwitterionic PI copolymer showed a two-stage weight loss curve. The initial weight loss around 300 ºC was assigned to the loss of the sulfonic acid and tertiary amine groups, and the second thermal degradation started from 500 ºC indicated the decomposition of the copolymer backbone. The TGA results listed in Table 1 clearly indicate that the zwitterionic PI copolymer has good thermal stability.

Table S1 Summary of the properties of the zwitterionic and reference PI copolymers.

Polymer	Feed (mol %)				Viscosity $\eta_{sp/c}$ (dL/g)	T_g (ºC)	$T_{5\%}$ (ºC)	$T_{10\%}$ (ºC)
	TPA-NMe$_2$	BAPBS	ODA	ODPA				
Zwitterionic PI	15	15	70	100	1.04	260.3	431.7	498.1
Reference PI	-	-	100	100	0.89	248.7	557.9	572.1

Figure Captions

Fig. S1 FTIR spectrum of diamine monomer BAPBS.

Fig. S2 ^{1}H NMR spectrum of diamine monomer BAPBS.

Fig. S3 FTIR spectrums of the zwitterionic and reference PI copolymers.

Fig. S4 ^{1}H NMR spectrums of the zwitterionic PI copolymer.

Fig. S5 DSC curves of the zwitterionic and reference PI copolymers.

Fig. S6 TGA curves of the zwitterionic and reference PI copolymers.