

pH-sensitive microfiltration membrane prepared from polyethersulfone grafted with poly(itaconic acid) synthesized by simultaneous irradiation in homogeneous phase

Kai Fan, Guoqing Zhou, Jinjin Zhang, Haijun Yang, Jun Hu and Zhengchi Hou

ABSTRACT

Poly(itaconic acid) (PIA) was grafted onto polyethersulfone (PES) by homogeneously phased γ -ray irradiation. Kinetic polymerization observed was studied by analyzing the effect of irradiation dosages and monomer concentrations. Then, a pH-sensitive microfiltration (MF) membrane was prepared from these PES-g-PIA polymers with different degrees of grafting under phase inversion method. Finally, the contact angles, morphologies, pore sizes, deionized water permeability and filtration performance for aqueous polyethylene glycols solution of the MF membranes were studied. The results show that grafting PIA groups onto PES molecular chains endowed the MF membranes with effective pH-sensitive properties.

Key words | graft polymerization, membrane, pH-sensitive, polyethersulfone, poly(itaconic acid)

Kai Fan
Guoqing Zhou
School of Architecture and Materials,
Chongqing College of Electronic Engineering,
Chongqing 401331,
China

Kai Fan
Jinjin Zhang
Haijun Yang
Jun Hu
Zhengchi Hou (corresponding author)
Division of Interfacial Water, CAS, Key Laboratory
of Interfacial Physics and Technology,
Shanghai Institute of Applied Physics, Chinese
Academy of Sciences,
Shanghai 201800,
China
E-mail: houzhengchi@sinap.ac.cn

HIGHLIGHTS

- Polyethersulfone grafted poly(itaconic acid) membrane with pH-sensitive performance
- Method of simultaneous γ -ray irradiation in homogeneous phase

INTRODUCTION

In recent years, polyethersulfone (PES), having outstanding chemical resistance and a high thermal stability performance, has become widely attractive as a material for microfiltration (MF) and ultrafiltration (UF) membranes (Van der Bruggen 2009; Zhao *et al.* 2013). Meanwhile, controlling the permeability and separation performance of PES membranes, functional groups like carboxyl and pyridine are introduced to endow these membranes with pH-responsive property, adaptive to their application environment (Zhao *et al.* 2011a, 2011b).

pH-sensitive membranes have been achieved by various different methods such as chemical grafts, physical blending, and surface-coating (Zhao *et al.* 2011a). For example, Bo Deng

and colleagues used γ -ray irradiation to graft poly(acrylic acid) and poly(methacrylic acid) (PMAA) onto the PES powder. The resulting pore sizes in the deionized water solution flux of the membranes prepared from these combinations demonstrated a corresponding relationship with pH values (Deng *et al.* 2008, 2009). Qing Shi and co-workers prepared identical PES-g-PMAA materials using a chemical polymerization method, and showed that these membranes also displayed an effective pH-sensitive performance (Shi *et al.* 2010).

However, we noticed that the solubility of the modified powder grafted through heterogeneous γ -ray irradiation copolymerization was poor in some normal organic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, especially for copolymers at high degrees of grafting (DGs), which was also mentioned in Deng *et al.* (2009, 2010).

Then we developed an innovative approach for copolymerization, referred to as homogeneously phased γ -ray irradiation. By using this method, we successfully grafted poly(methacrylic acid) onto PES molecular chains. The resulting copolymer proved to have a high solubility in organic solvents, and the

membranes cast from this modified polymer demonstrated effective pH dependent properties (Fan *et al.* 2017).

Itaconic acid (IA) as a characteristic monomer has found increasingly wide utilization in several methods of polymerization (Işıklan *et al.* 2011; Sakthivel *et al.* 2016). Due to the highly functional polarity and polyelectrolyte properties of carboxylic acid groups (–COOH) and acetic acid groups (–CH₂COOH) of poly(IA) in their molecular structures, it was generally believed that the grafting of poly(itaconic acid) (PIA) onto the matrix material will likely produce relatively pH-sensitive properties (Veličković *et al.* 1994; Tomić & Filipović 2004).

In this work, we have synthesized a pH-sensitive MF membrane by grafting PIAs onto PES molecular chains via homogeneously phased γ -ray irradiation. Kinetic polymerization was observed by analyzing the effect of irradiation dosages and monomer concentrations. This grafting reaction was confirmed by elemental analysis and infrared spectroscopy. Afterwards, PES-g-PIA with different DGs was used for preparing pH-sensitive MF membranes via the phase inversion method. Finally, the contact angles, morphologies, pore sizes, deionized water permeability and aqueous polyethylene glycols (PEG) solution, with different molecular weights, filtration performance of the MF membranes were studied. The results show that grafting PIA groups onto PES molecular chains endowed the MF membranes with effective pH-sensitive properties.

EXPERIMENT

Materials

PES powders (solid viscosity = 0.49 Pa·s) were purchased from Shandong Caihong Advanced Material Company (China), rinsed with 40 °C deionized water to remove impurities before use and then dried at 70 °C under vacuum until a constant weight was reached. IA, 1-methyl-2-pyrrolidone (NMP), polyvinylpyrrolidone (PVP) K30 (molecular weight = 50,000) and PEG with average molecular weights of 1, 6, 10, 20 and 35 kDa were purchased from Sinopharm Reagent Co. Ltd, China. Water purified by a Milli-Q system from Millipore™ was used for all experiments. Other materials mentioned above were used as purchased.

Radiation-induced graft polymerization

According to Table 1, mixtures of PES and N, N-dimethylformamide (DMF) were put into seven flasks and stirred for 24 hours at 60 °C to ensure complete assimilation of the PES

Table 1 | Quantity of materials used for synthesis of PES-g-PIA

Sample	IA/g	PES/g	DMF/g	Total/g
1	0.4	10	89.6	100
2	0.8	10	89.2	100
3	1.2	10	88.8	100
4	1.6	10	88.4	100
5	2.0	10	88	100
6	2.4	10	87.6	100
7	2.8	10	87.2	100

into the DMF solution. Then monomer IA was added into the mixture, after the samples were cooled down to room temperature, followed by stirring for an additional 3 hours until homogeneous solutions were achieved. After that, the mixtures were transferred into glass tubes, bubbled with nitrogen gas and sealed. The samples were then subjected to the γ -ray irradiation process at room temperature. To purify the grafted copolymers, these irradiated mixtures were then poured into water, where the PES-g-PIA products would quickly precipitate, being agitated in deionized (DI) water for 3 days. The DI water was refreshed every 6 hours to ensure the complete removal of homopolymer and organic solvents. Finally, the precipitate was dried at 70 °C under vacuum until the weight stabilized. The DG (%) of the PES-g-PIAs was determined by sulfur elemental analysis.

The DGs of samples were calculated with the following Equation (1):

$$DG (\%) = \frac{M_{PIA}}{M_{PES}} \times 100\% = \frac{\phi_I - \phi_{II}}{\phi_I} \times 100 \quad (1)$$

where M_{PIA} and M_{PES} are the molar mass of PIA and PES repeating unit respectively, ϕ_I and ϕ_{II} are the sulfur mass fraction in the PES powder before and after grafting copolymerization, respectively.

Infrared spectroscopy

Pristine and grafted PES-g-PIA were pressed into pellets with KBr for Fourier transform infrared (FT-IR) measurement using a Nicolet Avatar 370 FT-IR spectrometer with a culmination of 32 scans at a resolution of 4 cm⁻¹.

Membrane preparation

MF membranes were prepared by using a phase inversion method as follows.

Pristine PES or PES-g-PIA, PVP K30 and NMP solvents were mixed together at an 18:6:76 ratio. The mixtures were stirred at 60 °C for 3 days then allowed to rest at room temperature for 2 days. After that, the solutions were cast onto a glass plate by using a casting knife. And the resulting solution film on the glass plate was immersed in a water bath at 19 °C for several minutes until the membranes formed and automatically separated from the plate surface. The membranes were then immersed DI water refreshed every 6 hours for 2 days to remove any possible remaining solvents.

Contact angle measurements

Contact angle measurements of membranes were conducted on an Attension Theta System (KSV Instruments Ltd, Finland). A water droplet of approximately 5 µL was lowered onto the membrane surface with a needle. Then, a magnified image of the droplet was observed by a high definition digital camera. The static contact angles were determined, with the calculation software, from these images. For each sample, the measurement was repeated at least four times to calculate their average value as the contact angle.

Morphological study

Scanning electron microscopy (SEM) of surfaces and cross-sections of the membranes was carried out using a LEO1530vp scanning electron microscope (Germany), at a voltage of 10 kV at 10 mA. To obtain the cross-section images, the membranes were immersed in liquid nitrogen and fractured. These fractured samples were then attached to carbon tape and sprinkled with gold. The images were amplified to 800× to capture these cross-section images.

Pore size determination

Pore sizes of MF membranes were measured using the 'bubble point' analysis method on a custom-made device. Prior to the bubble point measurement, all MF membranes were immersed in solutions with prescribed pH values overnight. Then a membrane was mounted on the device with an effective area of 3.14 cm² to hold the samples. Nitrogen gas pressure was then gradually and continually increased. When the first bubble on the surface of the MF membrane was observed, the gas pressure was recorded, which indicates the largest pore size. When continuous bubbling was observed on the membrane's surface, the gas pressure was

recorded again, indicating the smallest pore sizes. The dependent pressure is described by the Washburn equation (Lei *et al.* 2003; Zhai *et al.* 2003; Sakthivel *et al.* 2017):

$$Pr = 2\gamma\cos\theta \quad (2)$$

where P is the N₂ pressure, r is the average pore radius of the measured sample, and $\gamma\cos\theta$ is the Wilhelmy plate surface tension.

Flux measurement

Membranes cast from the pristine PES and PES-g-PIA were cut to pieces with an effective area of 35.3 cm², which were mounted onto a Convergence Inspector-Poseidon device (Convergence Industry B. V. Holland) to measure their flux. The membrane surface velocity was set at 2 kg/hr and the operating pressure was configured at 0.5 bar. Before testing, membranes were kept in a continuous flow of water for 10 minutes to eliminate potential bubbles in the piping. The flux of aqueous water solutions with different pH values was automatically recorded by the flow meters in the Convergence Inspector device. The rejection was calculated by Equation (3):

$$R(\%) = 1 - \frac{C_p}{C_f} \times 100 \quad (3)$$

where C_p and C_f are the concentrations of the probe solute in permeate and feed respectively, which were determined by a total organic carbon analyzer (Shimadzu TOC-5000A).

During pH-sensitive permeability tests of membranes, the test membranes should be immersed in aqueous solutions with a specific pH value for at least 12 hours before testing, and then aqueous solutions with similar pH values were used to test the flux.

RESULTS AND DISCUSSION

Graft polymerization kinetics study

Figure 1(a) shows the effect of absorbed dosage on DG of PES-g-PIA. It should be noted that DG rose in correlation with the rise of the absorbed dosage while this value was below 18 kGy, reaching its maximum of approximately 7.56%. Then the DG appeared to gradually decrease as the apparent absorbed dosage increases. This result can likely be explained by the capability of the polymerization graft

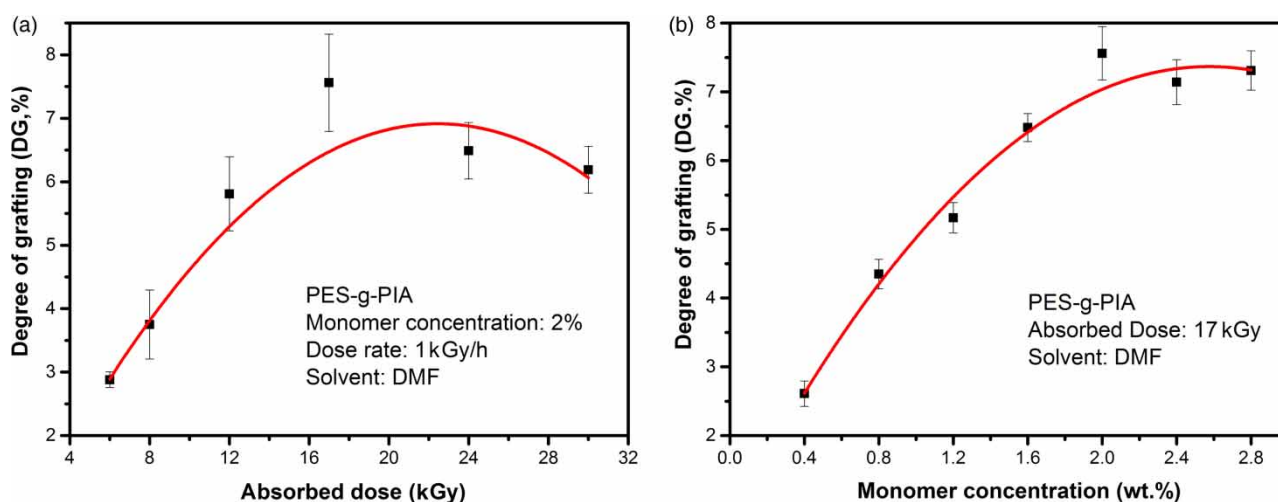


Figure 1 | Effect of (a) absorbed dose and (b) monomer concentrations on DG of PES-g-PIA.

of the PIA onto PES molecular chains, and the degradation of these PIA groups due to excessive γ -ray irradiation (Darville *et al.* 2003; Bhattacharya & Misra 2004). In the initial stage, monomer IA was initiated to graft under γ -ray irradiation and homopolymerized, forming a copolymer of PES-g-PIA. These two strong reactions at this stage resulted in an increased DG of the PES-g-PIA. However, further increases of absorbed dose irradiation on the crafted PES-g-PIA molecular chains may easily disintegrate the PIA chains in PES-g-PIA, resulting in a reduction of the DG.

Figure 1(b) demonstrates the effect of monomer concentration on the DGs of the PES-g-PIAs. DG increases with the monomer concentration below 2.0% then levels off. As we expect, this homogeneous phase system exemplifies the competition between grafting polymerization and homopolymerization caused by γ -ray irradiation. When the monomer concentration was lower than 2.0%, grafting polymerization dominates the whole reaction, resulting in an increase of DG. Further increasing the monomer concentration would enhance homopolymerization process much more than the grafting polymerization, resulting in a constant DG in the PES-g-PIA (Bhattacharya & Misra 2004; Nasef & Hegazy 2004).

FT-IR spectroscopy of the grafted copolymer

Figure 2 shows FT-IR spectra of the pristine PES and PES-g-PIA with different DGs, which clearly confirms that the chemical grafting of PIA onto PES molecular chains is effective. The exact information about FT-IR spectra of pristine

PES has been reported by many researchers (Li *et al.* 2006). Peaks at 1,323 and 1,300 cm^{-1} correspond to the asymmetric stretching vibration of the sulfone group. Aromatic skeletal vibrations at 1,577 cm^{-1} and stretching vibration at 1,485 cm^{-1} could be clearly observed as well; these two peak values were selected as the internal reference points we used to compare the differences between the spectra of pristine PES and of our samples of PES-g-PIAs with variant DG values. Notably, a new absorption band at 1,679 cm^{-1} appeared, which corresponds to the stretching vibrations of carbonyl groups ($-\text{C}=\text{O}-$), and was strengthened along with increasing the DGs of our PES-g-PIAs, indicating that PIA groups were successfully grafted onto the PES chains.

Contact angle measurements

It is generally accepted that an increased hydrophilicity of MF membranes could improve the anti-fouling abilities of membranes (Chen & Belfort 1999; Yang *et al.* 2005). An effective method to evaluate this property is to measure the contact angle of membranes. Figure 3 shows contact angles of membranes made from PES-g-PIA with different DG values. The decrease of the contact angle of MF membranes was obviously observed while increasing the DG value of the PES-g-PIA. This result illustrates a considerable improvement in the hydrophilicity of membranes with increased DG values of PES-g-PIA. Therefore, the grafting of PIA onto PES chains by γ -ray irradiation in a homogeneous phase was an effective method to improve the hydrophilicity of MF membranes.

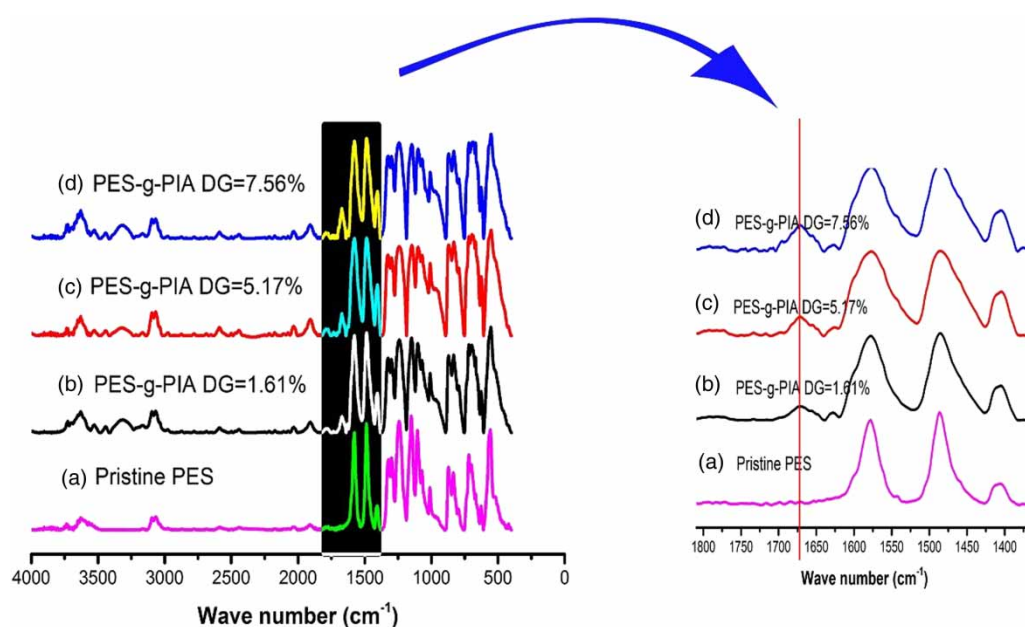


Figure 2 | FT-IR spectra of (a) pristine PES and PES-g-PIA with DGs of (b) 1.61%, (c) 5.17%, (d) 7.56%.

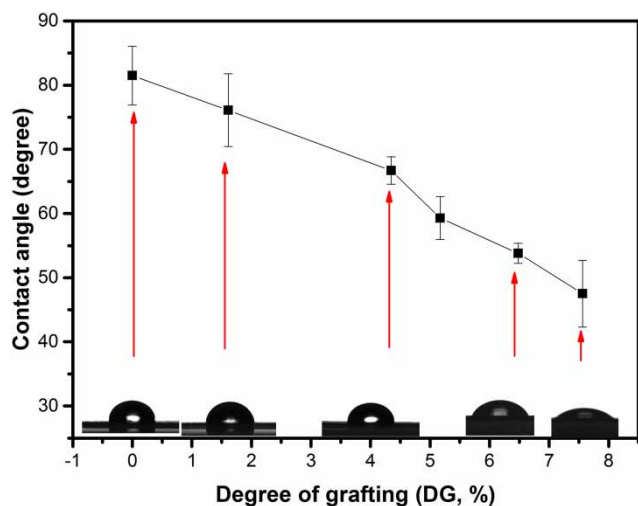


Figure 3 | Shows the corresponding relationships between the different DG values of PES-g-PIA, and the contact angles of the respective membranes.

Cross-sectional structure analysis

It is generally agreed that the parameters of interaction between graft copolymer and organic solvent (Flory-Huggins parameter), as well as graft copolymer itself, impacts the formation of membrane (Rana *et al.* 1993, 1996a, 1996b) (Boom *et al.* 1992; Smolders *et al.* 1992). These parameters are different for pristine PES versus the modified PES polymers, which affect the process of dry-wet phase separation, producing different membrane

structures. The cross-sectional SEM morphology of pristine PES membrane and different DGs of PES-g-PIA membranes is shown in Figure 4. It is easy to see that all of the samples display an asymmetric membrane, due to the phase inversion method. Meanwhile, the sub-layer of the pristine PES MF membrane and PES-g-PIA MF membrane demonstrates a progressive transformation: the sub-layer of MF membranes show a trend from a figure-like structure of pristine PES membrane to a sponge-like structure of PES-g-PIA membrane. As DG value of PES-g-PIA increased, there was the formation of some 'big holes' in this sponge-like structure, and these 'big holes' continuously swelled.

These singular structures in morphology could probably be explained by the variations of the performance dynamics during the formation of the membranes, which is caused by the grafting of a PIA onto PES molecular chains (Strathmann & Kock 1977). In the rapid demixing protocol, the required demixing time (the delay time) is controlled by the mutual diffusion rate between the solvents and non-solvents. During the process of demixing in a sub-layer, the pristine PES/solvent/water process displayed an instantaneous liquid-liquid (L-L) demixing resulting in a finger-like structure. In contrast, the PES-g-PIA/solvent/water process remains thermodynamically stable, which means that the diffusion rate was relatively lower than the pristine PES/solvent/water procedure. This delayed L-L demixing performance seriously affected the sub-layer's formation and resulted in a sponge-like structure.

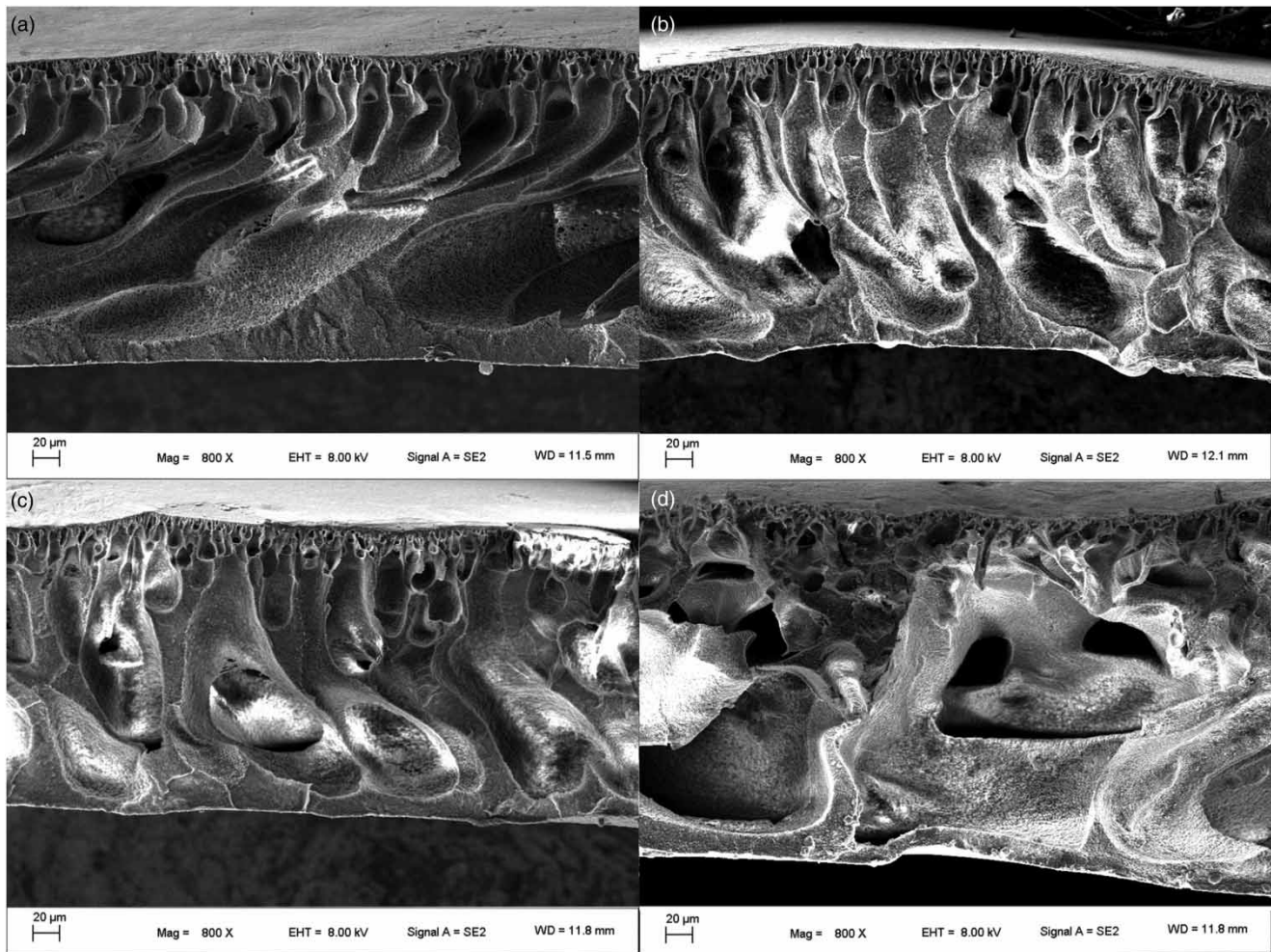


Figure 4 | Cross-sectional SEM morphology images of (a) pristine PES membrane, (b) PES-g-PIA with DG of 1.61% membrane, (c) PES-g-PIA with DG of 5.17% membrane, and (d) PES-g-PIA with DG of 7.56% membrane.

Pore size analysis

The mean pore size of four typical MF membranes (pristine PES, PES-g-PIA with DG of 1.61%, PES-g-PIA with DG of 5.17% and PES-g-PIA with DG of 7.56%) at different pH values is presented in Figure 5. It can be noticed that, with the increase in DGs of the PES-g-PIAs, the pore size of corresponding membranes decreased. A reasonable explanation could be that the PIA chains are seemingly more flexible than the PES chains; grafting PIAs onto the PES chains likely reduces the interspaces within the original PES chains. The pore size of the ‘network pore’ shrinks constantly with an increasing DG value of PES-g-PIA (Ying *et al.* 2002; Fan *et al.* 2017).

Meanwhile, the mean pore size of MF membranes cast from pristine PES indicates an independence from the pH value and remains stable at about 52 nm. In contrast,

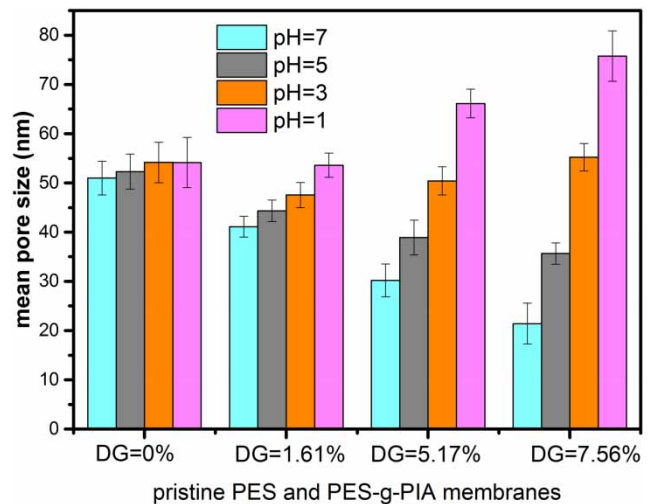


Figure 5 | Mean pore sizes of pristine PES and different DG valued PES-g-PIA MF membranes at various pH values.

the pore sizes of the PES-g-PIA membranes show consistent pH-sensitive variation, which changes exponentially at a higher DG values. This phenomenon demonstrates an interesting ‘intelligent like’ quality to the pH-sensitivity performance of the modified membranes.

Deionized water flux performance of MF membranes at different pH value

Figure 6(a) shows the pH-sensitive deionized water flux of the pristine PES and PES-g-PIA membranes at different DG values. It was discovered that the water flux of the pristine PES membrane was virtually constant (approximately 148.3 L/m²·h) at various pH values, whereas the flux of the aqueous water solution through the PES-g-PIA membranes decreases with the increase of the pH value. The water flux of a membrane made from PES-g-PIA with a DG of 7.56% at a pH value of 1 increases by about 33.7% compared to that of the same membrane at pH value of 7. This result evinces that grafting PIAs onto PES chains endows the resulting membrane with a pH-sensitive property, which is consistent with the results revealed by the mean pore sizes of the MF membranes.

A reversible test of the membranes constituted from pristine PES and PES-g-PIA with a DG of 7.56% was carried out by switching solution pH value at 1.0 and 7.0 multiple times to test pH-sensitive consistency. The results can be seen in Figure 6(b). The water flux of the pristine PES membrane was unchanged after repeated variations of the pH values. Contrarily, water flux of the pH-sensitive PES-g-PIA

membranes with a DG of 7.56% was nearly instantaneous and completely reversible.

The pH-sensitive property of MF membranes can be quantitatively described by the Hagen–Poiseuille law (Lee & Jin 1997). Water flux of a porous membrane is generally governed by the fourth power of the pore diameter. Thus, the pH-sensitive properties of the membranes are directly related to the membrane’s permeability performance. A higher DG value of PES-g-PIA corresponds to a greater variation of the permeability at different pH values.

Filtration performance of MF membranes

It is generally understood that, the molecular weight cutoff (MWCO) is one of the most important specifications to describe the retention capabilities of membranes. It could represent the pore size variations during changes in the solute pH values, since a higher MWCO is believed to correspond to larger pore sizes (Zhou *et al.* 2010; Shen *et al.* 2015). To further study the pH-sensitive properties of the modified membranes, rejection of solutes different molecular weights at different pH values for PES-g-PIA membranes with a DG value of 7.56% was tested, as shown in Figure 7. It can be seen that the rejection performance tends to increase at higher pH value for a given molecular weight composition. Interestingly, the discrimination at a higher pH value is better than at a lower pH value, which means that the pore size of this MF would shrink at higher pH values, consistent with the trend of pore size variations as before mentioned in the section ‘pore size analysis’.

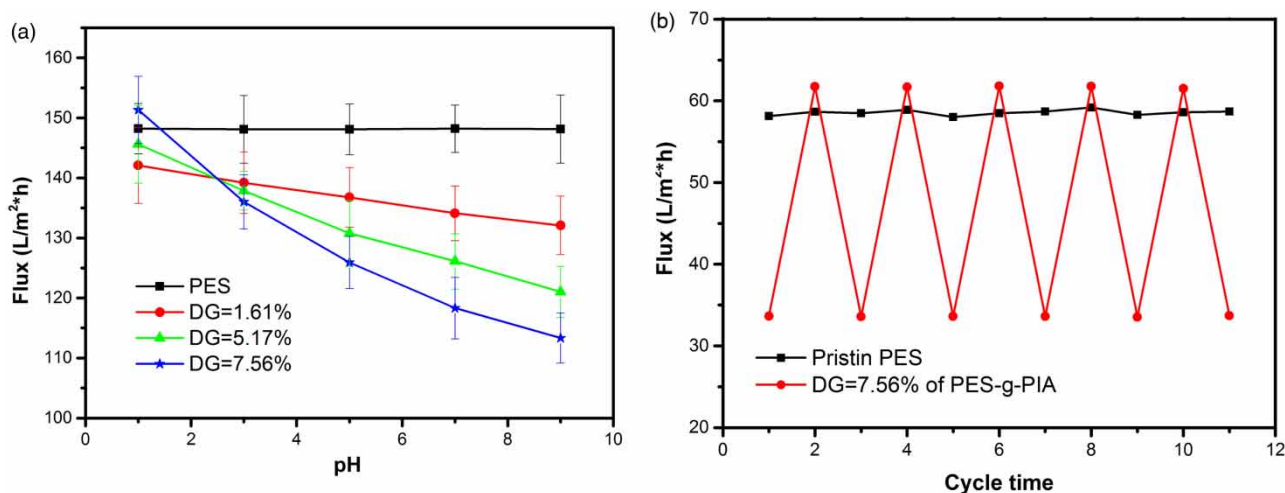


Figure 6 | (a) Respective relationships between pH value and deionized water fluxes of membranes cast from pristine PES, PES-g-PIA with DG values at 1.61%, 5.17% and 7.56%. (b) Reversible test of deionized water permeability performance at pH values of 1 and 7 using MF membrane of pristine PES and PES-g-PIA with a DG of 7.56%.

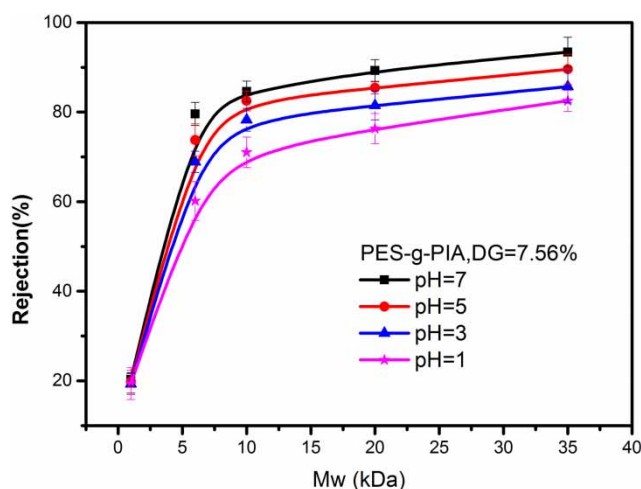


Figure 7 | Rejection curves of MF membranes prepared from PES-g-PIA with a DG of 7.56% at pH values of 7, 5, 3 and 1.

CONCLUSION

In this work, PIAs were successfully grafted onto PES chains using simultaneous irradiation in a homogeneous phase. Graft polymerization kinetics were investigated and the grafted products were analyzed by FT-IR. Pristine PES and synthesized PES-g-PIAs were then completely dissolved in organic solvents and incorporated into MF membranes through the phase inversion method. Then, the contact angles of MF membranes were tested, showing a uniform increase of hydrophilicity with the rise of DG values of the PES-g-PIA. The morphology of the MF membranes shows that the grafted PIA on PES chains tended to form sponge-like structures in the sub-layer of the membrane. Then, pore size, water flux and aqueous PEG solution filtration performance of the MF membranes were tested. Due to polyelectrolyte groups of PIA grafted onto PES molecular chains, these modified membranes demonstrated pH-sensitive performances, while the pristine PES membranes did not. Finally these pH-sensitive properties were tested repeatedly and confirmed by testing the filtration performance of the MF membrane for aqueous PEG solution.

ACKNOWLEDGEMENT

This work was financially supported by the National Natural Foundation of China (Grant No. 11375252, U1632135); the CAS Key Research Program of Frontier Sciences (Grant No. QYZDJ-SSW-SLH019).

REFERENCES

- Bhattacharya, A. & Misra, B. N. 2004 Grafting: a versatile means to modify polymers: techniques, factors and applications. *Progress in Polymer Science* **29** (8), 767–814.
- Boom, R. M., Wienk, I. M., Boomgaard, T. v. d. & Smolders, C. A. 1992 Microstructures in phase inversion membranes. Part 2. The role of a polymeric additive. *Journal of Membrane Science* **73** (2–3), 277–292.
- Chen, H. & Belfort, G. 1999 Surface modification of poly(ether sulfone) ultrafiltration membranes by low-temperature plasma-induced graft polymerization. *Journal of Applied Polymer Science* **72** (13), 1699–1711.
- Dargaville, T. R., George, G. A., Hill, D. J. T. & Whittaker, A. K. 2003 High energy radiation grafting of fluoropolymers. *Progress in Polymer Science* **28** (9), 1355–1376.
- Deng, B., Li, J., Hou, Z., Yao, S., Shi, L., Liang, G. & Sheng, K. 2008 Microfiltration membranes prepared from polyethersulfone powder grafted with acrylic acid by simultaneous irradiation and their pH dependence. *Radiation Physics and Chemistry* **77** (7), 898–906.
- Deng, B., Yang, X., Xie, L., Li, J., Hou, Z., Yao, S., Liang, G., Sheng, K. & Huang, Q. 2009 Microfiltration membranes with pH dependent property prepared from poly(methacrylic acid) grafted polyethersulfone powder. *Journal of Membrane Science* **330** (1–2), 363–368.
- Deng, B., Yu, M., Yang, X., Zhang, B., Li, L., Xie, L., Li, J. & Lu, X. 2010 Antifouling microfiltration membranes prepared from acrylic acid or methacrylic acid grafted poly(vinylidene fluoride) powder synthesized via pre-irradiation induced graft polymerization. *Journal of Membrane Science* **350** (1–2), 252–258.
- Fan, K., Huang, J., Yang, H., Lu, R., Sun, X., Hu, J. & Hou, Z. 2017 pH and thermal-dependent ultrafiltration membranes prepared from poly(methacrylic acid) grafted onto polyethersulfone synthesized by simultaneous irradiation in homogenous phase. *Journal of Membrane Science* **543**, 335–341.
- Işiklan, N., İnal, M., Kurşun, F. & Ercan, G. 2011 pH responsive itaconic acid grafted alginate microspheres for the controlled release of nifedipine. *Carbohydrate Polymers* **84** (3), 933–943.
- Lee, Y. M. & Jin, K. S. 1997 Preparation of pH/temperature responsive polymer membrane by plasma polymerization and its riboflavin permeation. *Polymer* **38** (5), 1227–1232.
- Lei, Y., Kang, E. T. & Neoh, K. G. 2003 Characterization of membranes prepared from blends of poly(acrylic acid)-graft-poly(vinylidene fluoride) with poly(N-isopropylacrylamide) and their temperature- and pH-sensitive microfiltration. *Journal of Membrane Science* **224** (1–2), 93–106.
- Li, J., Oshima, A., Miura, T. & Washio, M. 2006 Preparation of the crosslinked polyethersulfone films by high-temperature electron-beam irradiation. *Polymer Degradation & Stability* **91** (12), 2867–2873.
- Nasef, M. M. & Hegazy, E.-S. A. 2004 Preparation and applications of ion exchange membranes by radiation-induced graft copolymerization of polar monomers onto non-polar films. *Progress in Polymer Science* **29** (6), 499–561.

- Rana, D., Mandal, B. M. & Bhattacharyya, S. N. 1993 Miscibility and phase diagrams of poly(phenyl acrylate) and poly(styrene-co-acrylonitrile) blends. *Polymer* **34** (7), 1454–1459.
- Rana, D., And, B. M. M. & Bhattacharyya, S. N. 1996a Analogue calorimetric studies of blends of poly(vinyl ester)s and polyacrylates. *Macromolecules* **29** (5), 1579–1583.
- Rana, D., Mandal, B. M. & Bhattacharyya, S. N. 1996b Analogue calorimetry of polymer blends: poly(styrene-co-acrylonitrile) and poly(phenyl acrylate) or poly(vinyl benzoate). *Polymer* **37** (12), 2439–2443.
- Sakthivel, M., Franklin, D. S. & Guhanathan, S. 2016 pH-sensitive itaconic acid based polymeric hydrogels for dye removal applications. *Ecotoxicology and Environmental Safety* **134** (Pt 2), 427–432.
- Sakthivel, M., Franklin, D. S., Sudarsan, S., Chitra, G. & Guhanathan, S. 2017 Investigation on Au-nano incorporated pH-sensitive (itaconic acid/acrylic acid/triethylene glycol) based polymeric biocompatible hydrogels. *Materials Science and Engineering: C: Materials for Biological Applications* **75**, 517–523.
- Shen, L., Li, L., Chen, J., Hong, H., Yu, H., Hou, Z., Lin, H. & Lu, X. 2015 Effects of molecular weight distribution (M_w) on the performances of the polyethersulfone (PES) ultrafiltration membranes. *Journal of Membrane Science* **490**, 220–226.
- Shi, Q., Su, Y., Ning, X., Chen, W., Peng, J. & Jiang, Z. 2010 Graft polymerization of methacrylic acid onto polyethersulfone for potential pH-responsive membrane materials. *Journal of Membrane Science* **347** (1–2), 62–68.
- Smolders, C. A., Reuvers, A. J., Boom, R. M. & Wienk, I. M. 1992 Microstructures in phase-inversion membranes. Part 1. Formation of macrovoids. *Journal of Membrane Science* **73** (2), 259–275.
- Strathmann, H. & Kock, K. 1977 The formation mechanism of phase inversion membranes. *Desalination* **21** (3), 241–255.
- Tomić, S. L. & Filipović, J. M. 2004 Synthesis and characterization of complexes between poly(itaconic acid) and poly(ethylene glycol). *Polymer Bulletin* **52** (5), 355–364.
- Van der Bruggen, B. 2009 Chemical modification of polyethersulfone nanofiltration membranes: a review. *Journal of Applied Polymer Science* **114** (1), 630–642.
- Veličković, J., Filipović, J. & Djakov, D. P. 1994 The synthesis and characterization of poly(itaconic) acid. *Polymer Bulletin* **32** (2), 169–172.
- Yang, Q., Xu, Z., Dai, Z., Wang, J. & Ulbricht, M. 2005 Surface modification of polypropylene microporous membranes with a novel glycopolymer. *Chemistry of Materials* **17** (11), 3050–3058.
- Ying, L., Kang, E. T. & Neoh, K. G. 2002 Covalent immobilization of glucose oxidase on microporous membranes prepared from poly(vinylidene fluoride) with grafted poly(acrylic acid) side chains. *Journal of Membrane Science* **208** (1), 361–374.
- Zhai, G., Kang, E. T. & Neoh, K. G. 2003 Poly(2-vinylpyridine)- and poly(4-vinylpyridine)-graft-poly(vinylidene fluoride) copolymers and their pH-sensitive microfiltration membranes. *Journal of Membrane Science* **217** (1–2), 243–259.
- Zhao, C., Nie, S., Tang, M. & Sun, S. 2011a Polymeric pH-sensitive membranes – a review. *Progress in Polymer Science* **36** (11), 1499–1520.
- Zhao, X., Su, Y., Chen, W., Peng, J. & Jiang, Z. 2011b pH-responsive and fouling-release properties of PES ultrafiltration membranes modified by multi-functional block-like copolymers. *Journal of Membrane Science* **382** (1–2), 222–230.
- Zhao, C., Xue, J., Ran, F. & Sun, S. 2013 Modification of polyethersulfone membranes – a review of methods. *Progress in Materials Science* **58** (1), 76–150.
- Zhou, C., Hou, Z., Lu, X., Liu, Z., Bian, X., Shi, L. & Li, L. 2010 Effect of polyethersulfone molecular weight on structure and performance of ultrafiltration membranes. *Industrial & Engineering Chemistry Research* **49** (20), 9988–9997.

First received 5 March 2018; accepted in revised form 13 July 2018. Available online 1 August 2018