

## Introduction

Membrane materials play a significant role in the pervaporation process. As far as polymeric membranes are concerned, both their chemical and aggregation structures are equally important in determining their physical properties and separation performances. Polyelectrolyte complexes (PECs), representing a type of multi-component polymeric material with broad applications, were formed by electrostatic complexation between oppositely charged polyelectrolytes. PECs have been proved as a promising candidate for pervaporation dehydration of alcohols. PEC membranes (PECMs) with different chemical structures exhibited a wide variation of performance. It inspired us to further regulate the separation performance of PECM by tailoring the side chains of the cationic polyelectrolyte while maintaining similar polymer backbones. Meanwhile, the correlation between the chemical structures and aggregation structures was performed by molecular dynamics (MD) simulation and positron annihilation lifetime spectroscopy (PAS).

## Experimental

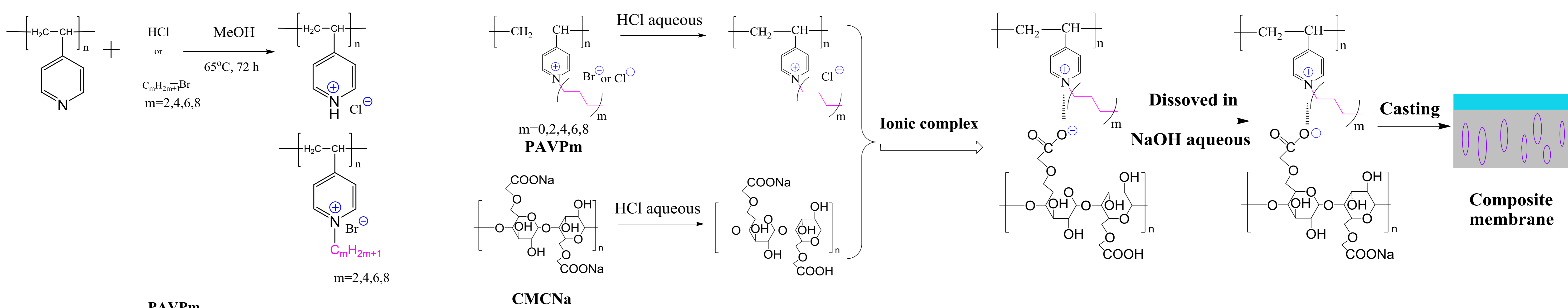


Fig. 1 Schematic of synthesis of PAVPm, PECs and PECMs.

## Results and discussion

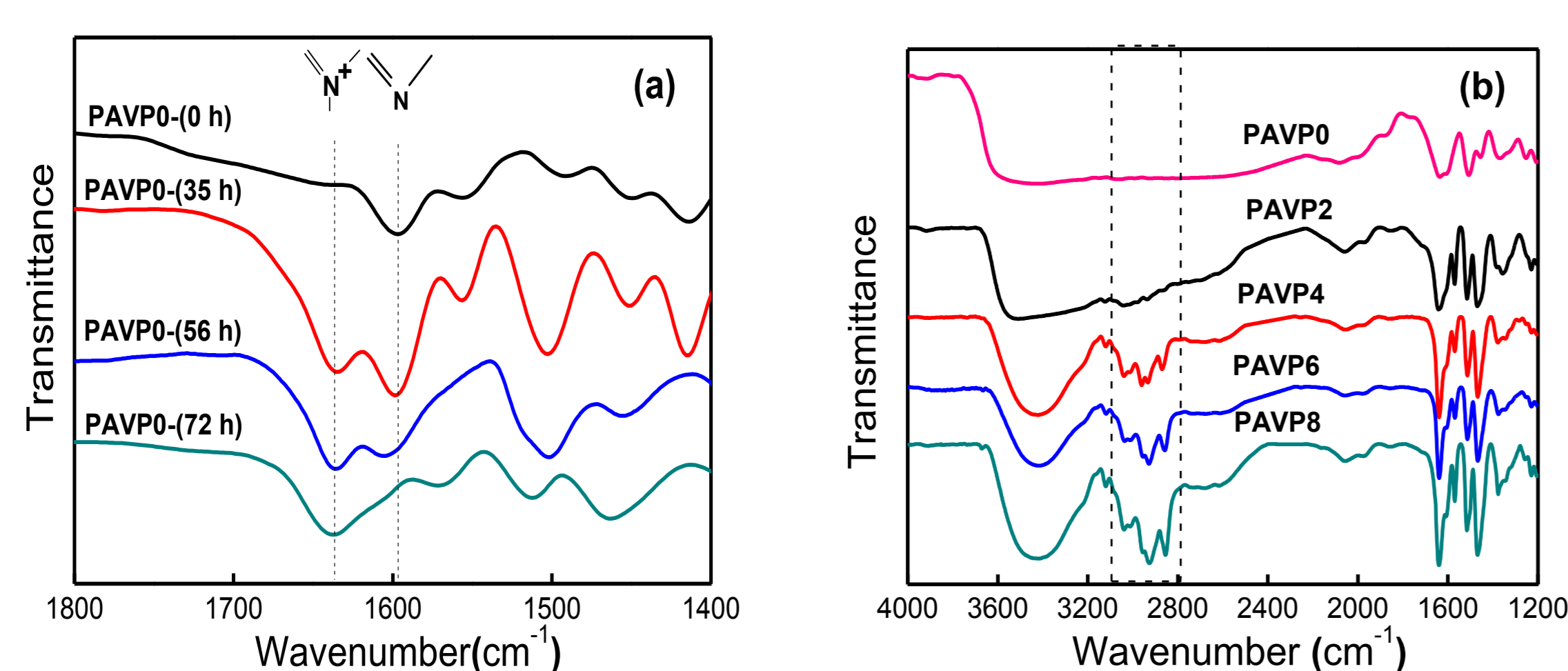


Fig. 2. FT-IR spectra of (a) PAVP0 quaternized by HCl for different times; (b) PAVPm quaternized by different alkali halides for 72 h.

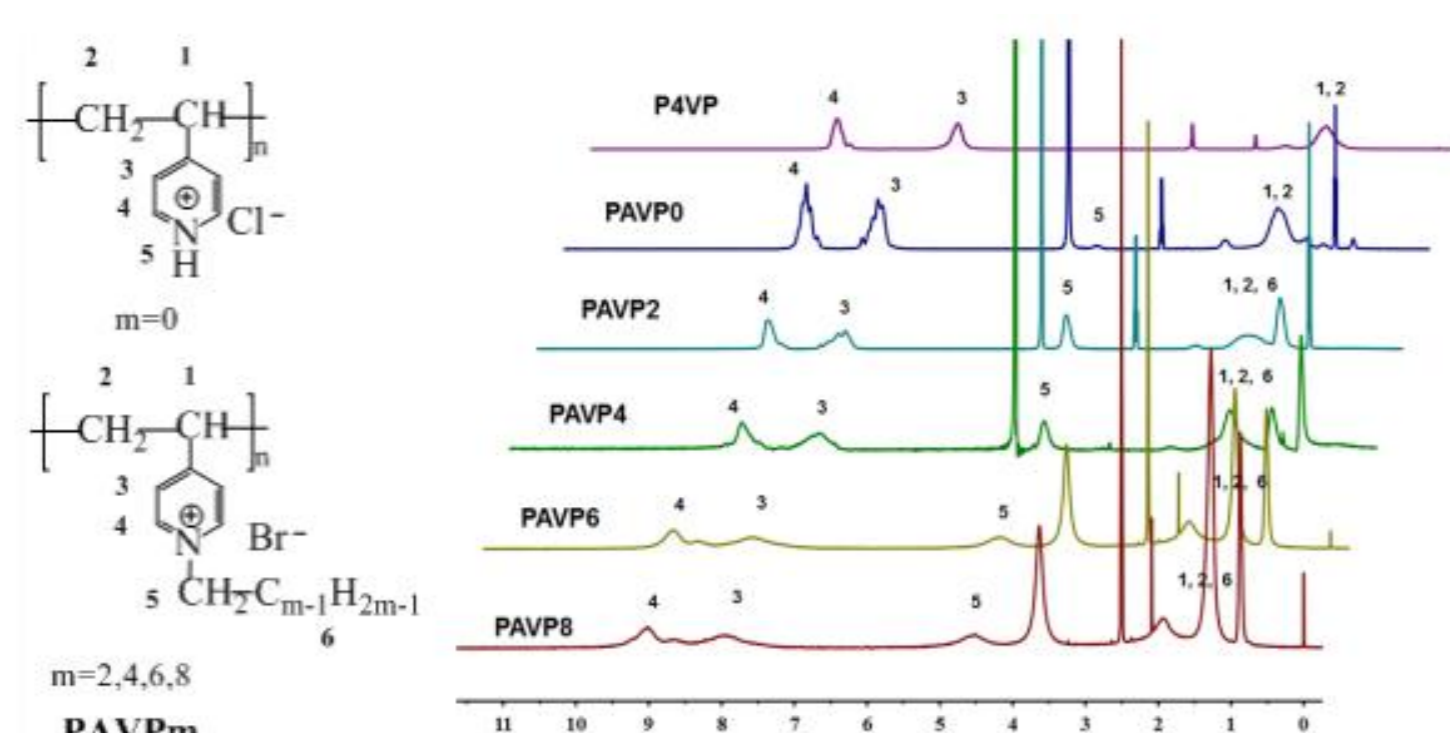


Fig. 3. <sup>1</sup>H NMR for P4VP and PAVPm.

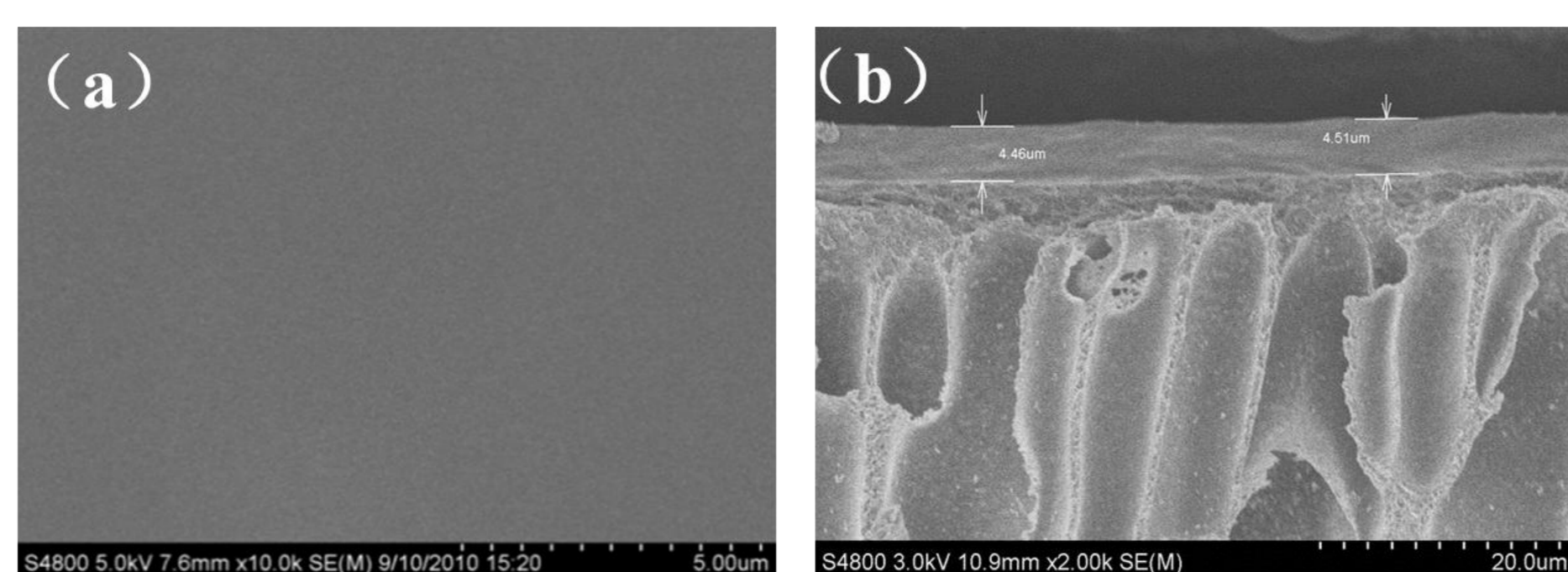


Fig. 4. SEM morphology of PECM surface (a) and cross section (b).

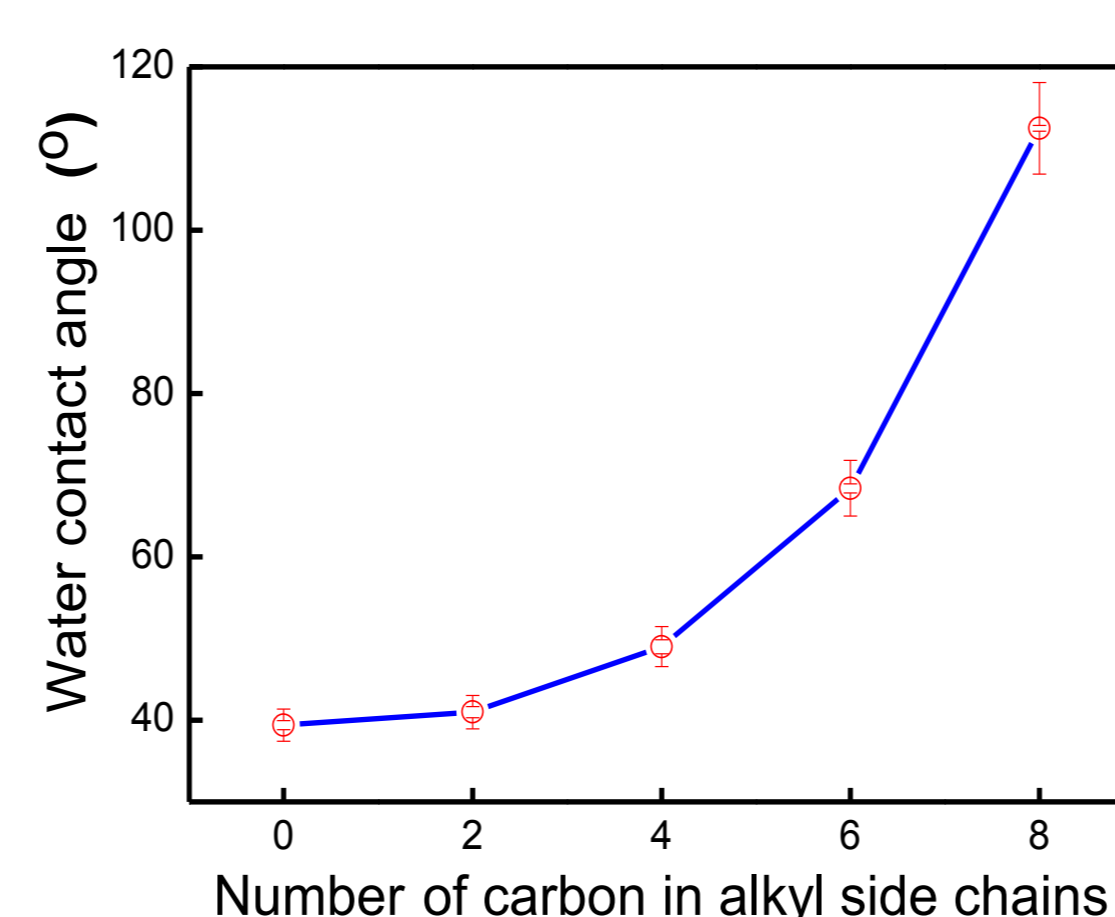


Fig. 5. Effect of the alkyl side chain length on water contact angles of PECMs.

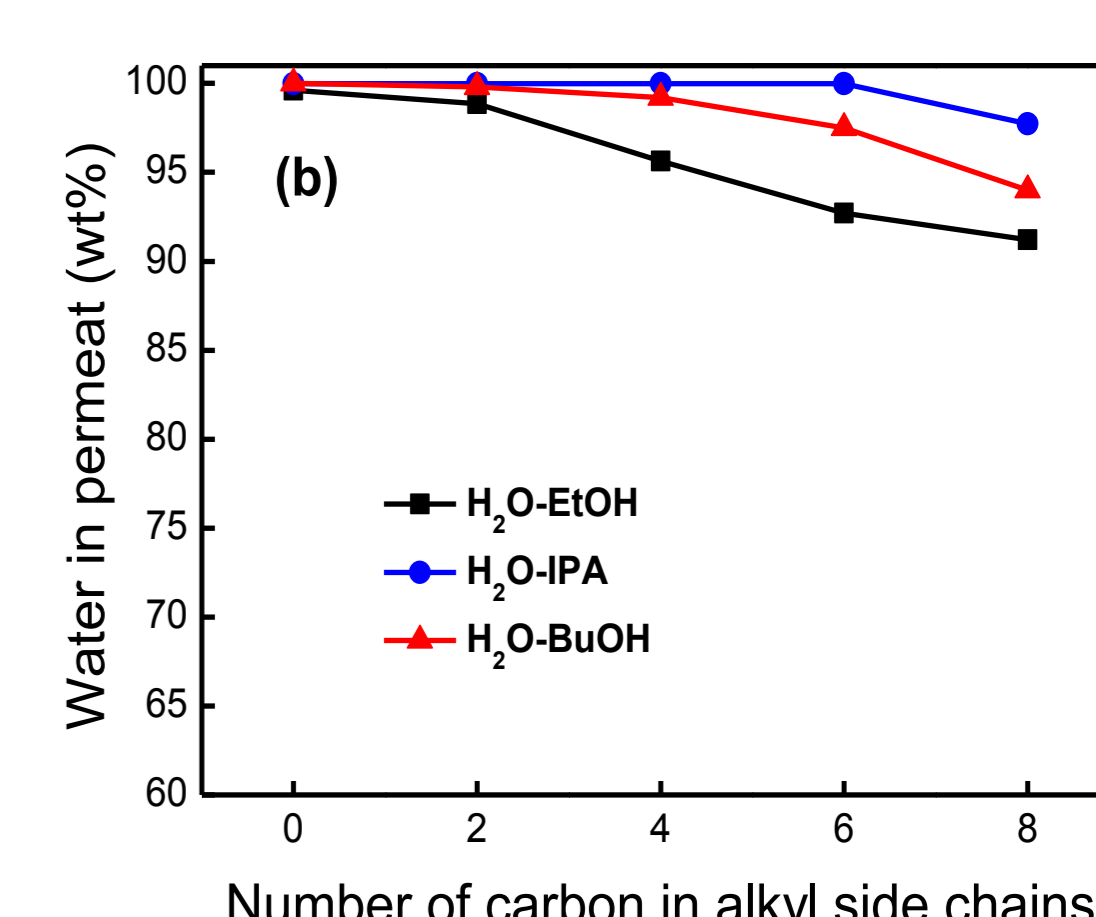
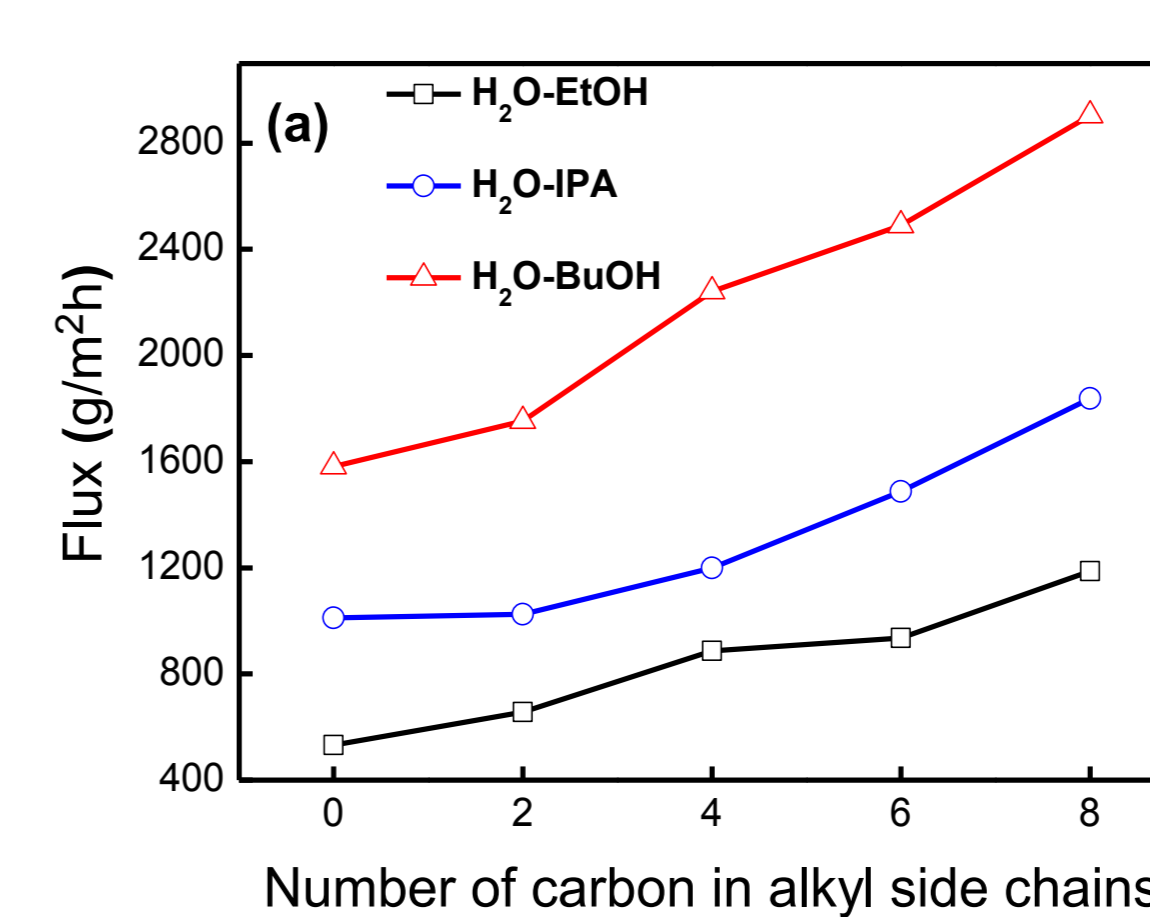


Fig. 6. Effect of the side chain length on the pervaporation performance of PECMs in separating 10 wt% H<sub>2</sub>O-EtOH, H<sub>2</sub>O-IPA and H<sub>2</sub>O-BuOH mixtures at 60 °C, flux (a) and water in permeate (b).

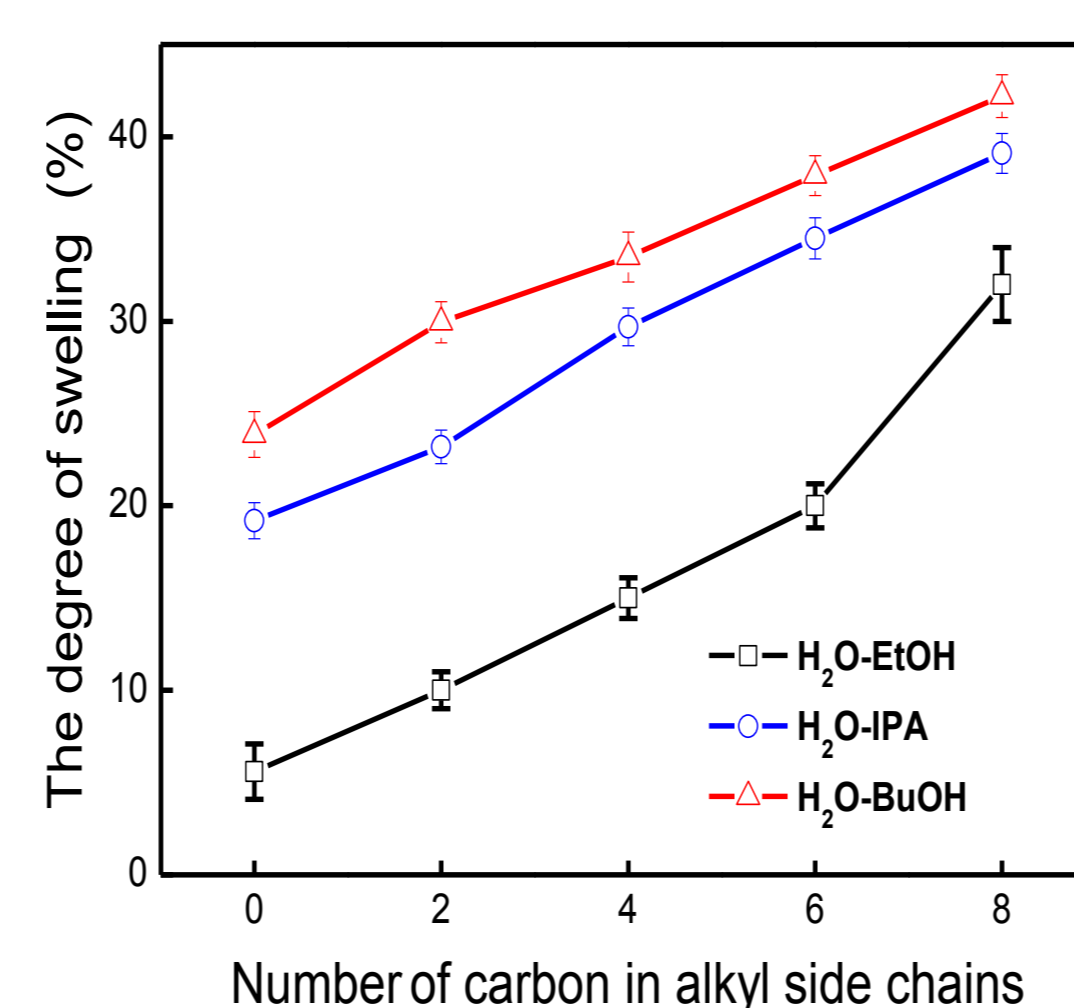


Fig. 7. The degree of swelling of PECMs in 10 wt% H<sub>2</sub>O-EtOH, H<sub>2</sub>O-IPA and H<sub>2</sub>O-BuOH solutions at 60 °C.

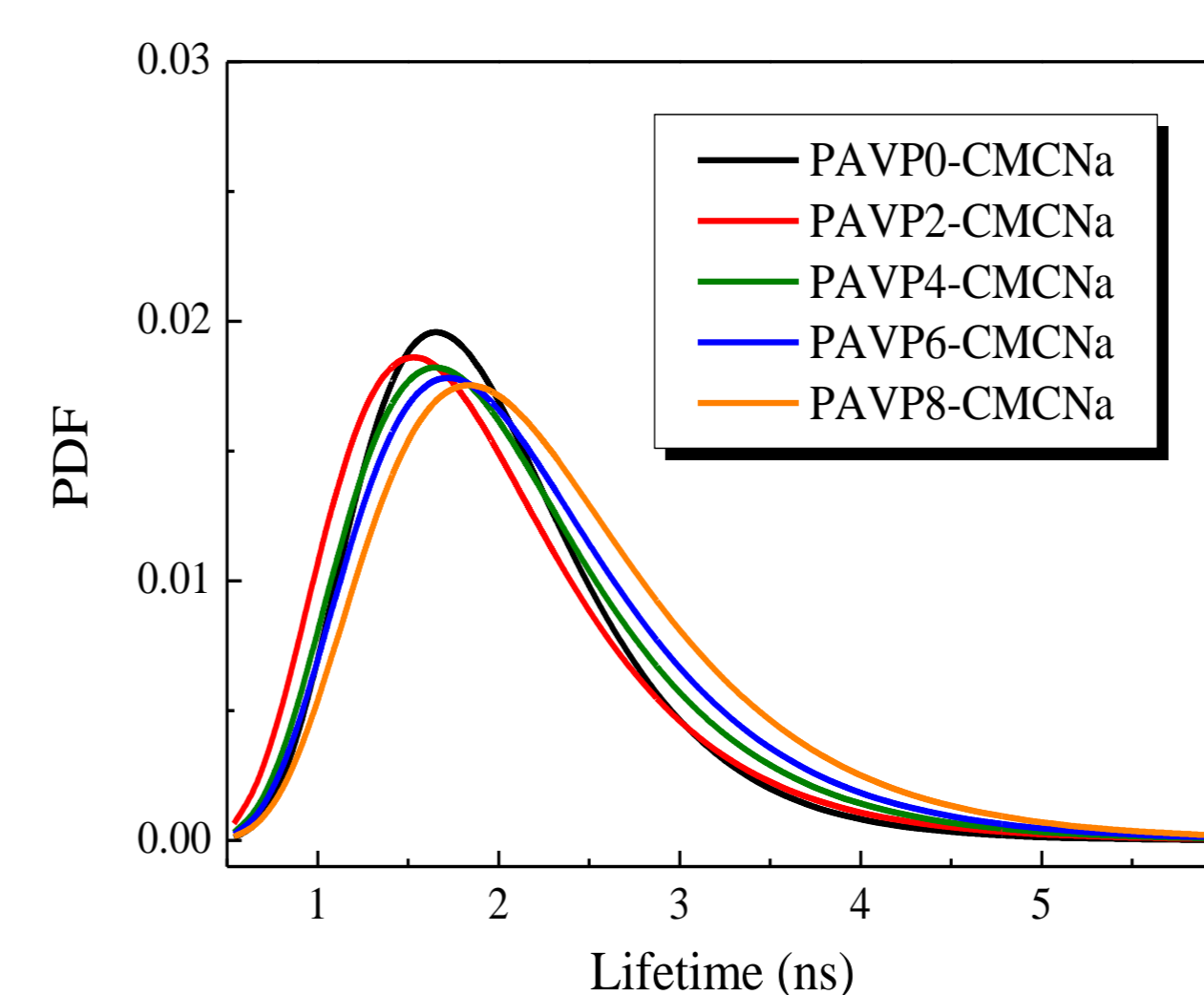


Fig. 8. o-Ps lifetime distribution data for PECMs.

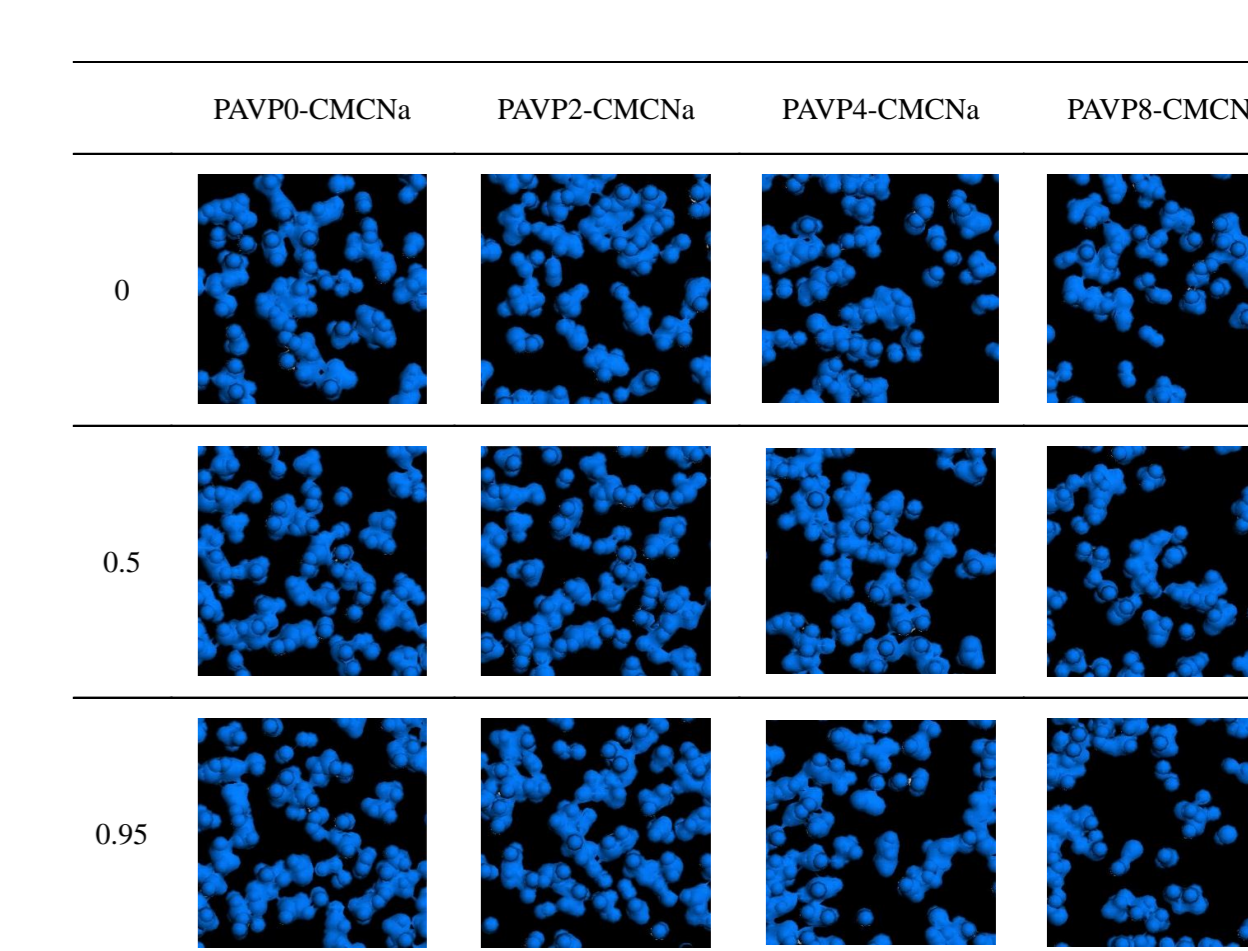


Fig. 9. Free-volume in a cross-sectional image segment of a PECM model; each segment has a thickness of 1.5 Å. (Blue color region refers to polymer chains and the black color to the free-volume).

## Conclusions

- PECMs with different alkyl groups were prepared for dehydration of different alcohols. Separation performance of PECMs could be tailored via altering the side chains length.
- Microstructure varied in PECMs was tunable to the pervaporation process. PAS and MD techniques showed good correlation with the pervaporation performance.

## References

1. T. Liu, Q.F. An, K.R. Lee, etc., *J. Membr. Sci.* 2013, 429(1-2): 181-189.
2. Y.H. Huang, Q.F. An, T. Liu, etc., *J. Membr. Sci.* 2013.

## Acknowledgements

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