Electronic Supplementary Material (ESI) for RSC Advances

Molecular Modelling of Polyimides with Intrinsic Microporosity: From Structural Characteristics to Transport Behaviour

Supplementary Information:

Physical Property Analysis

Sorption Analysis

The process of gas molecule sorption in a membrane can be divided into the three following steps: (1) the molecule is absorbed in the membrane matrix, (2) the absorbate reacts or exchanges sorption sites in the membrane matrix, and (3) the absorbate desorbs from the membrane matrix. In the present work, MC simulations were used to correctly calculate and illustrate the three sorption mechanisms. Here, the sorption interface behaviours were simulated using the grand canonical Monte Carlo method (GCMC). In addition, the gas concentration probability in the membrane matrix was determined using the energy change between the new configuration and the previous configuration. In this procedure, the acceptance or rejection of the configurational movements of the sorbate molecules was decided using the Metropolis algorithm. There are four types of configurational movements, including creation, rotation, translation, and destruction. The creation and destruction probabilities of the movements of the sorbate molecules can be expressed as

$$P = \min\left[1; \exp\left(-\frac{\Delta E}{kT} \pm \ln\frac{(N_i+1)kT}{f_i V}\right)\right], \quad (1)$$

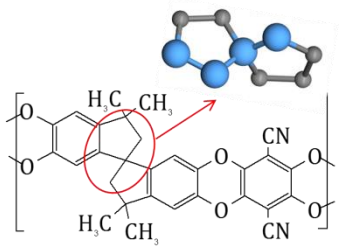
where ΔE is the energy change between the new configuration and the previous configuration, k is Boltzmann's constant, T is the assigned simulation temperature, N_i is the number of the component

i molecule in the configuration, *f* is the fugacity of the component *i* molecule, and *V* is the cell volume. The probability of translational movement in the membrane cell is

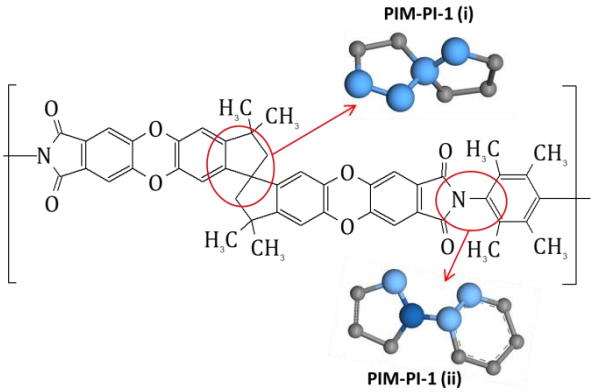
$$P = \min\left[1; \exp\left(-\frac{\Delta E}{kT}\right)\right]. \quad (2)$$

All four types of the aforementioned probabilities were calculated and considered as a complete MC calculation step. The sorption analysis calculation in this work was processed 5,000,000 times. The number of accepted sorption configurations was recorded and calculated as the sorption loading.

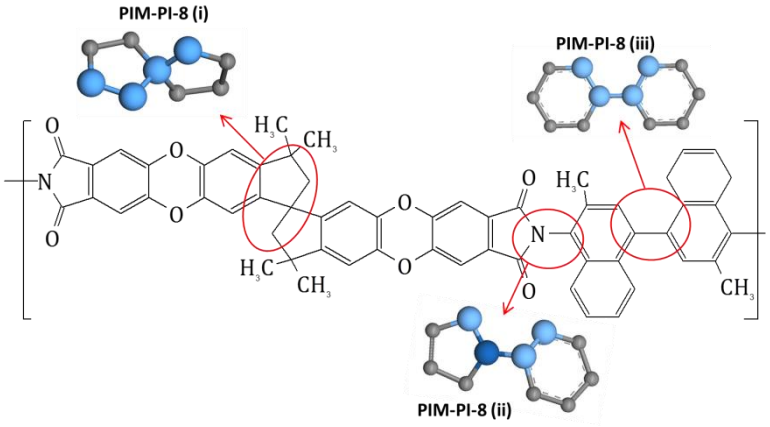
Torsional Angle Distributions



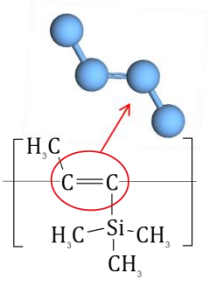
(a) PIM-1



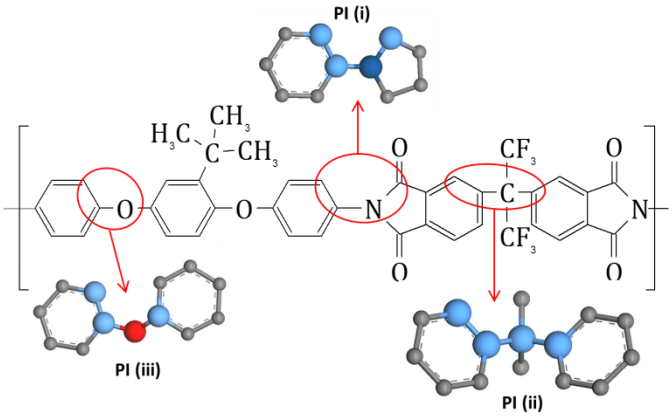
(b) PIM-PI-1



(c) PIM-PI-8



(d) PTMSP



(e) PI

Simulated and Experimental Values of Diffusivity and Permeability

Diffusivity

Table S1 Simulated and experimental diffusivities of four kinds of gas in the membranes.

	Simulated diffusivity (10^{-8} ·cm^2 /s)			
	CO_2	CH_4	O_2	N_2
PIM-1	75.28±5.34	64.30±28.46	213.16±52.80	123.87±28.56
PIM-PI-1	27.46±11	19.97±8.40	72.56±28.56	39.19±16.77
PIM-PI-8	71.96±39.22	24.07±13.81	101.95±31.44	53.43±16.38
PTMSP	5739.74±433.84	8782.01±1333.11	10323.80±876.47	10486.07±3764.44
PI	17.07±3.54	8.57±3.13	29.88±12.66	7.90±3.05

	Experimental diffusivity (10^{-8} ·cm^2 /s)			
	CO_2	CH_4	O_2	N_2
PIM-1[1]	160	71	390	160
PIM-PI-1[2]	17	7	56	20
PIM-PI-8[2]	45	14	130	41
PTMSP[3]	2640	2640	4650	3500
PI	-	-	-	-

Permeability

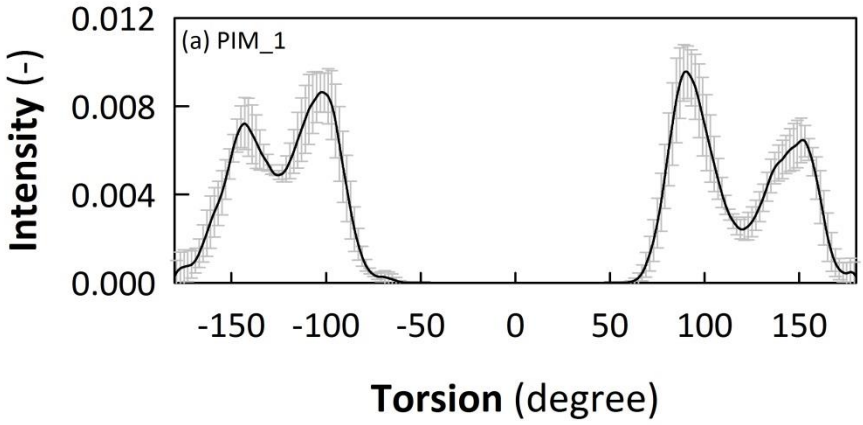
Table S2 Simulated and experimental permeabilities of four kinds of gas in the membranes.

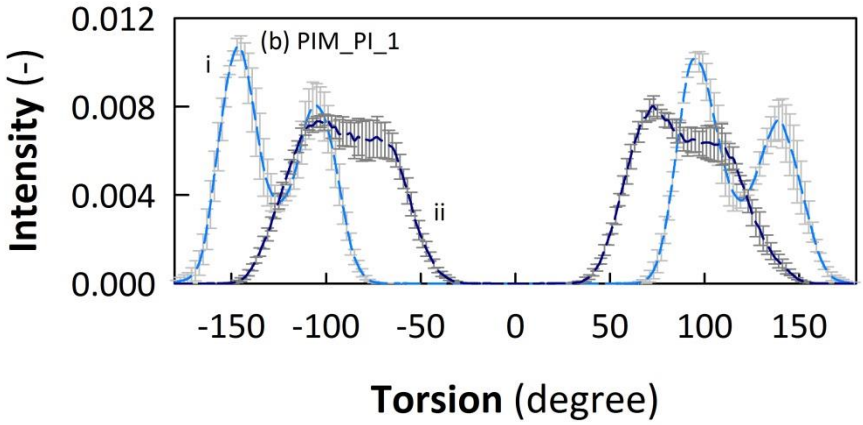
	Simulated permeability (Barrer)			
	CO_2	CH_4	O_2	N_2
PIM-1	3199.19	546.58	1172.40	396.37
PIM-PI-1	950.10	197.72	377.29	137.16
PIM-PI-8	1480.93	257.54	560.72	213.74
PTMSP	51083.71	50935.67	30971.40	25166.56
PI	288.4374	41.99	86.66	14.23

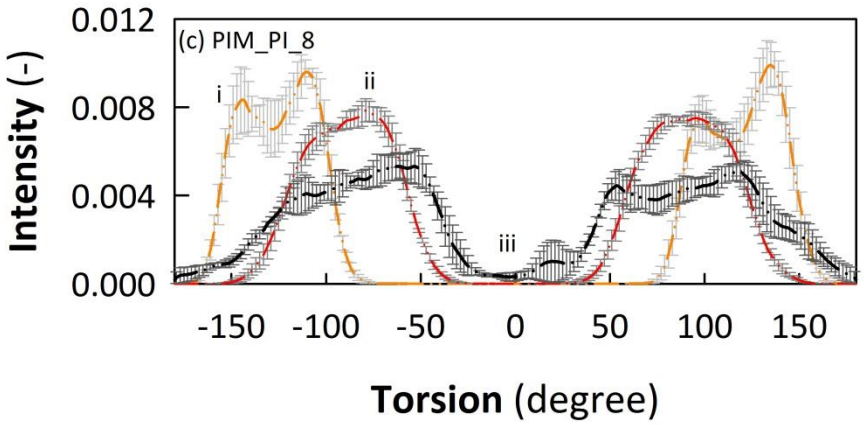
	Experimental permeability (Barrer)			
	CO_2	CH_4	O_2	N_2
PIM-1[1]	11200	1160	1530	610
PIM-PI-1[2]	1100	77	150	47
PIM-PI-8[2]	3700	260	545	160
PTMSP[3]	27984	12936	7905	4900
PI[4]	-	-	7.70	2.56.

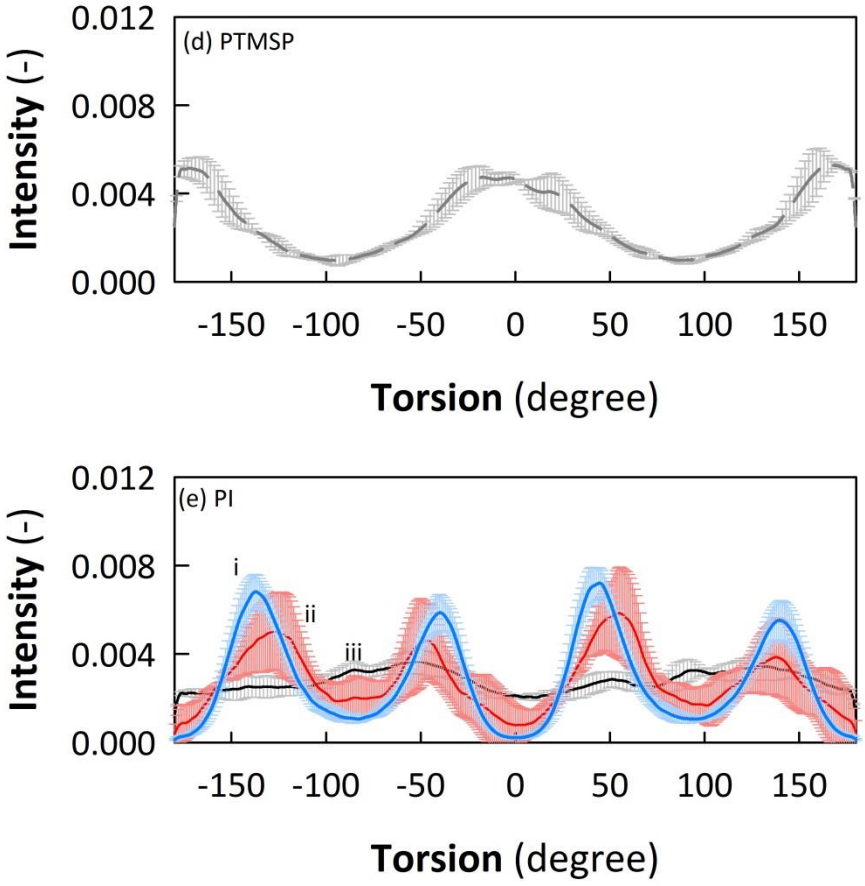
Results with Error Bars

The Dihedral Angle Distribution

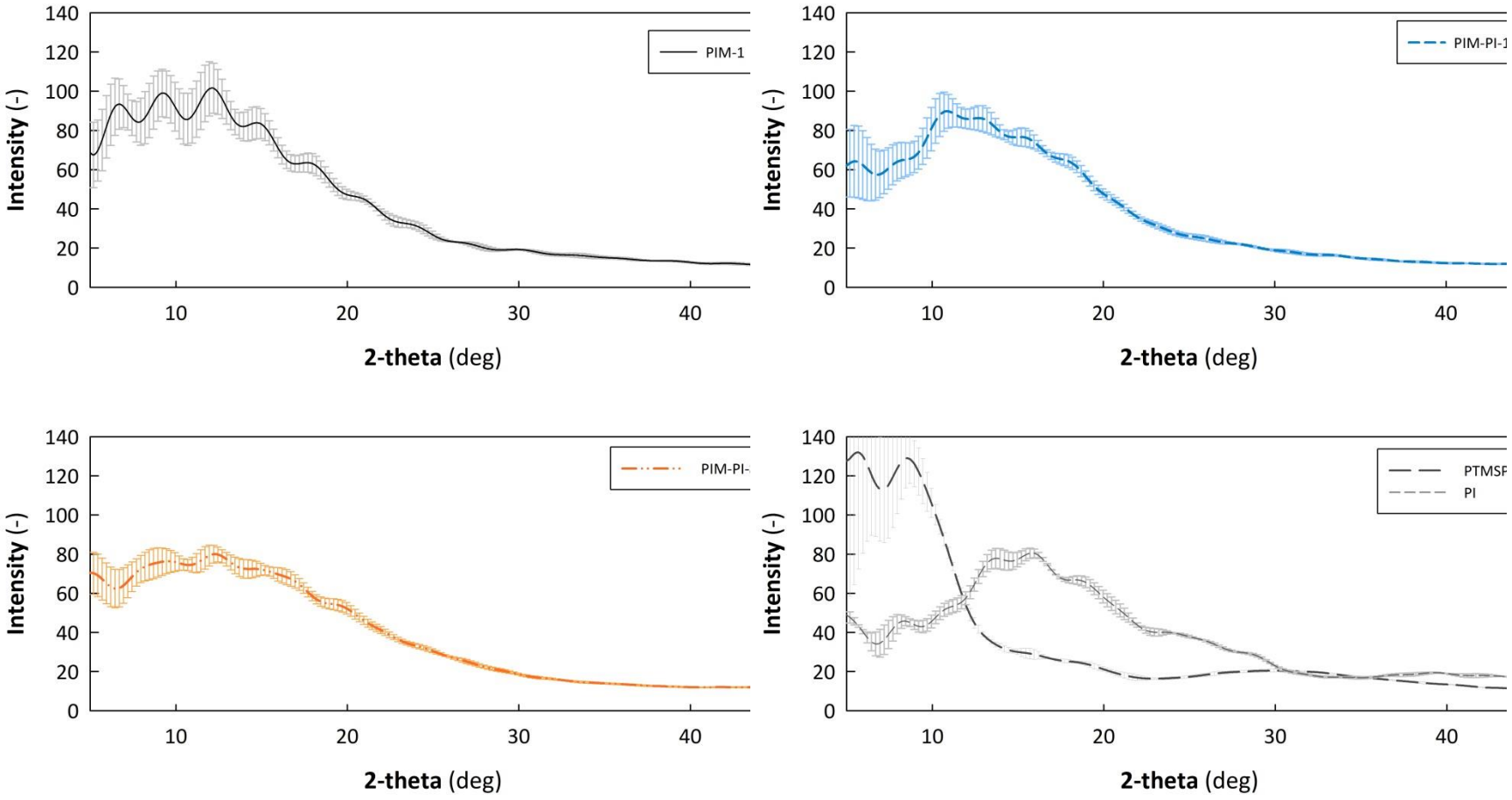




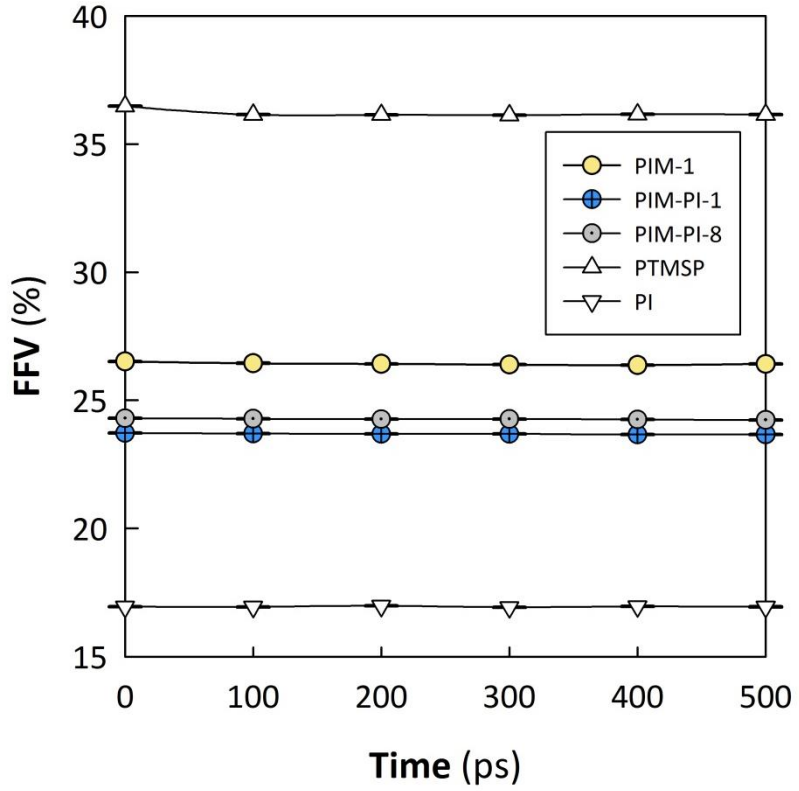


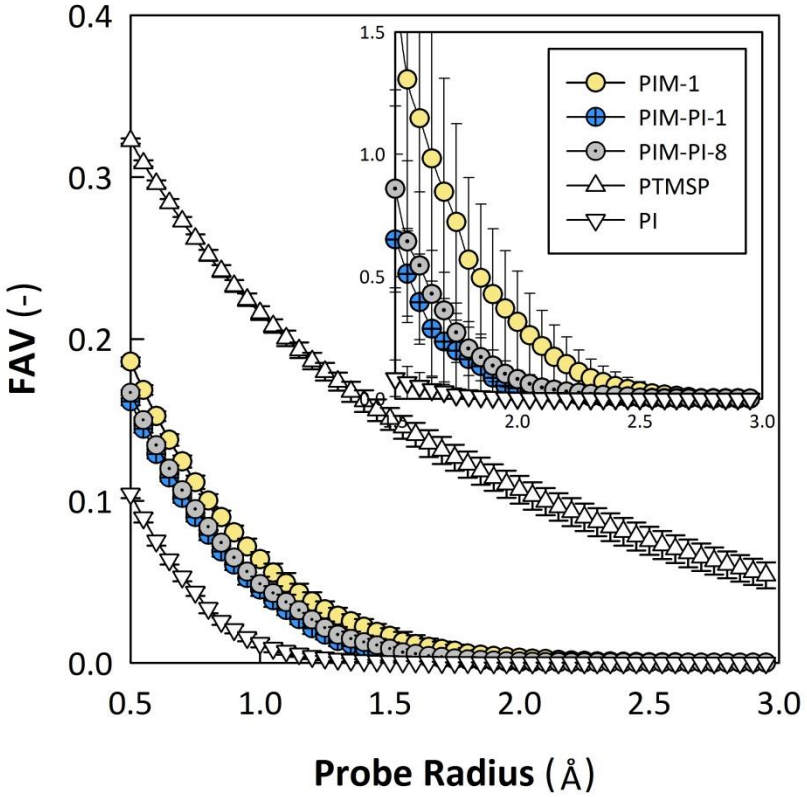


Simulated WAXD diagrams

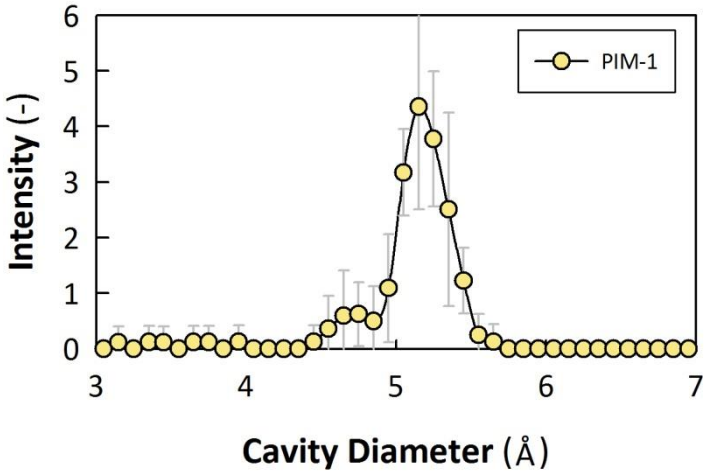


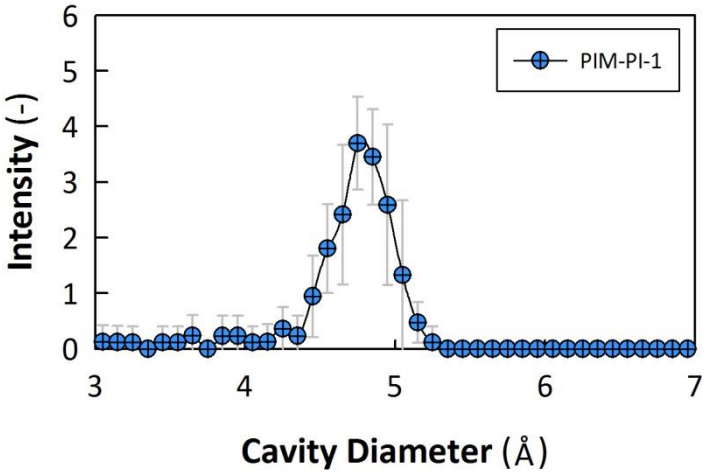
FFV and FAV

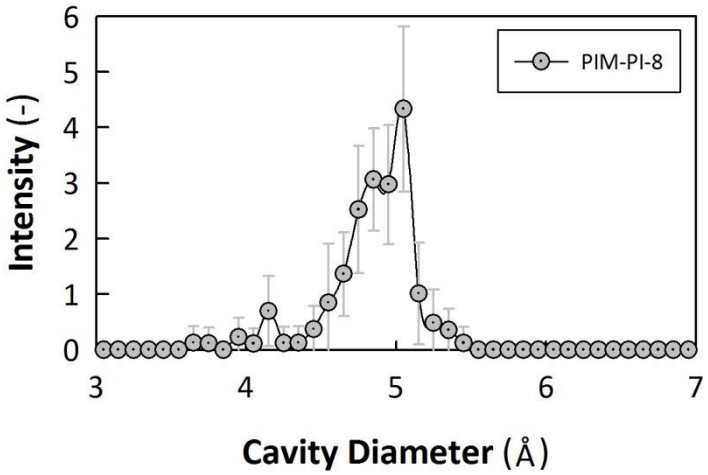


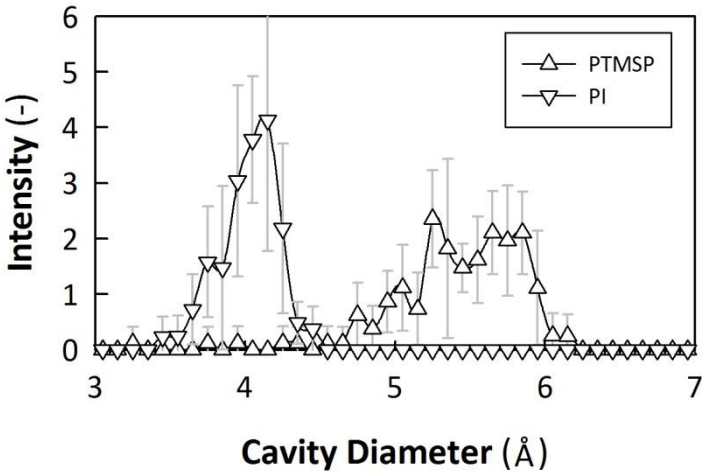


Cavity size distributions









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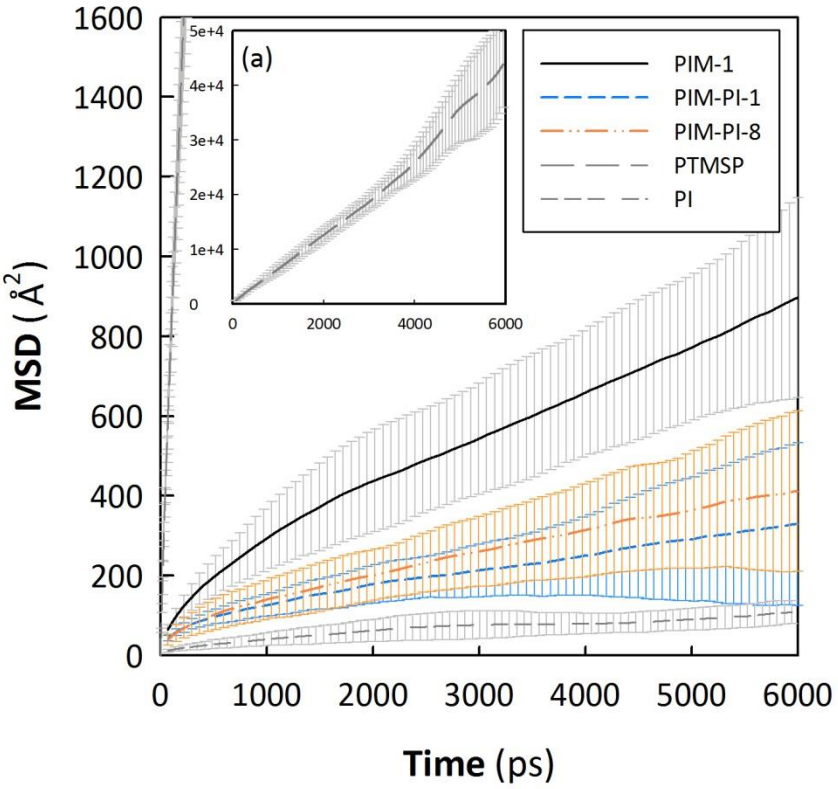
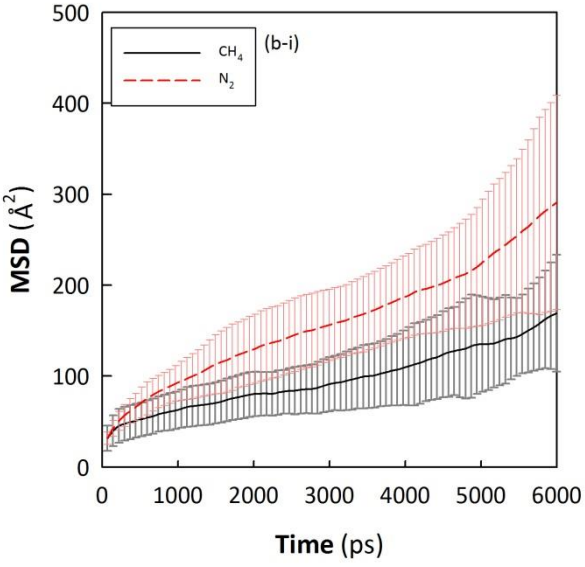
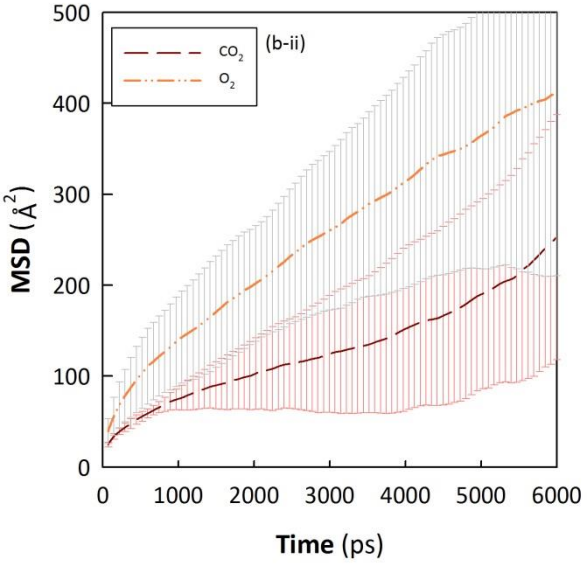
MSD diagrams







References

1. P. M. Budd, N. B. McKeown, B. S. Ghanem, K. J. Msayib, D. Fritsch, L. Starannikova, N. Belov, O. Sanfirova, Y. Yampolskii and V. Shantarovich, *J. Membr. Sci.*, 2008, **325**, 851-860.
2. B. S. Ghanem, N. B. McKeown, P. M. Budd, J. D. Selbie and D. Fritsch, *Adv. Mater.*, 2008, **20**, 2766-2771.
3. D. Hofmann, M. Heuchel, Y. Yampolskii, V. Khotimskii and V. Shantarovich, *Macromolecules*, 2002, **35**, 2129-2140.
4. Y.-C. Wang, S.-H. Huang, C.-C. Hu, C.-L. Li, K.-R. Lee, D.-J. Liaw and J.-Y. Lai, *J. Membr. Sci.*, 2005, **248**, 15-25.