Electronic Supplementary Material (ESI) for RSC Advances.

Polymer chain length, phosphoric acid doping and temperature dependence on structure and dynamics of ABPBI [poly(2,5-benzimidazole)] polymer electrolyte membrane

Minal More[‡a], *Anurag Prakash Sunda*[‡b] *and Arun Venkatnathan*[a]*

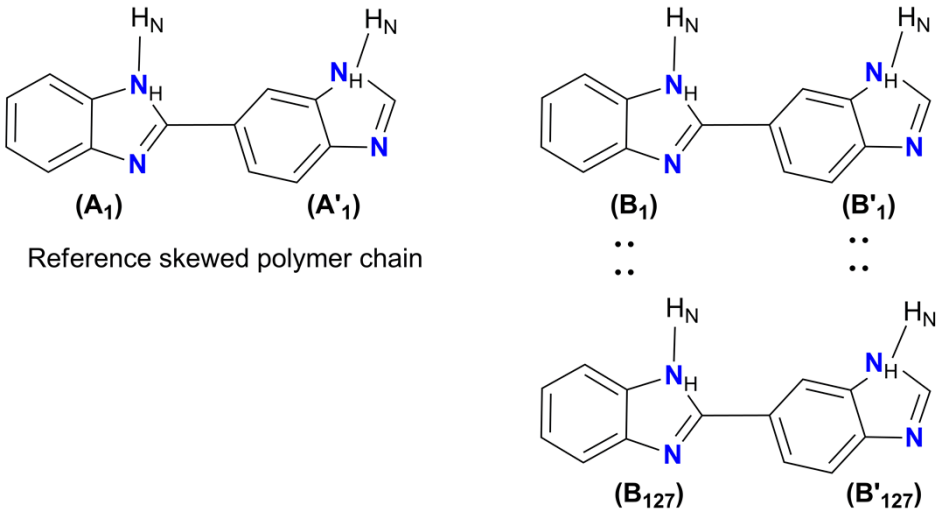
[a]Department of Chemistry, Indian Institute of Science Education and Research, Pune-411008, India.

[b]Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore-560064, India.

(‡Equal contribution; *Corresponding Author)

Cluster analysis around the benzimidazole (BI) moiety:

The BI_{com}-BI_{com} RDF is calculated using an average of RDFs in following manner: We first choose a skewed configuration (lowest Rg) as a reference polymer chain. Each BI_{com}-BI_{com} RDF is calculated between the center of mass of a BI unit of the reference polymer chain and the center of mass of every BI unit of all other polymer chains. For e. g. in a dimer, the BI_{com}-BI_{com} RDF is calculated between the center of mass of each BI unit of the reference polymer chain and the center of mass of each BI unit of 127 ABPBI polymer chains. This leads to four possibilities of RDFs such as: $\{(A_1, B_{1\text{-}127}), (A_1, B'_{1\text{-}127}), (A'_1, B_{1\text{-}127}), (A'_1, B'_{1\text{-}127})\}$



Thus, the final BI_{com}-BI_{com} RDF is calculated from an average of these four BI_{com}-BI_{com} RDFs in a dimer. Similarly, the BI_{com}-BI_{com} RDFs in a trimer, tetramer, pentamer, and decamer is calculated as an average of 9, 16, 25 and 100 BI_{com}-BI_{com} RDFs respectively.

Table S1: Diffusion coefficients (D_A) from a 10 ns production run.

Polymer Chain length	PA doping (γ)	D_A of PA (× 10^{-7} cm^2 sec^{-1})			
		300 K	350 K	400 K	450 K
Dimer (n=2)	1.6	0.0137	0.0314	0.1676	1.3010
	3.0	0.0222	0.0630	0.4812	2.3701
	3.7	0.0276	0.0714	0.4241	2.5001
Trimer (n=3)	1.6	0.0171	0.0463	0.2520	1.4201
	3.0	0.0217	0.0648	0.4497	1.9901
	3.7	0.0205	0.0762	0.4276	2.3101
Tetramer (n=4)	1.6	0.0164	0.0492	0.1927	1.1901
	3.0	0.0214	0.0564	0.4039	2.0810
	3.7	0.0266	0.0699	0.5532	2.5110
Pentamer (n=5)	1.6	0.0174	0.0424	0.1614	1.1201
	3.0	0.0250	0.0807	0.4568	2.2001
	3.7	0.0209	0.0847	0.5329	2.6401
Decamer (n=10)	1.6	0.0212	0.0439	0.1741	0.8332
	3.0	0.0307	0.0865	0.3801	1.9701
	3.7	0.0247	0.0813	0.5073	2.3801

Table S2: Average density (g cm^{-3}), end-to-end polymer chain distance ($\bar{R}_{E-E}$), radius of gyration ($\bar{R}g$) and Diffusion coefficients ($D_A \times 10^{-7}$ cm^2 sec^{-1}) of PA (γ=1.6) in PA doped ABPBI membrane.

System	Decamer (n=10)		Hectamer (n=100)	
Temperature	300 K	450 K	300 K	450 K
Density (g cm^{-3})	1.59	1.57	1.62	1.57
$\bar{R}_{E-E}$ (Å)	28.15 ± 9.20	28.55 ± 8.59	48.66 ± 12.68	48.95 ± 13.58
$\bar{R}g$ (Å)	11.15 ± 1.69	11.30 ± 1.72	14.91 ± 0.89	15.11 ± 0.85
D_A of PA	0.02 ± 0.01	0.83 ± 0.05	0.01 ± 0.01	1.23 ± 0.06

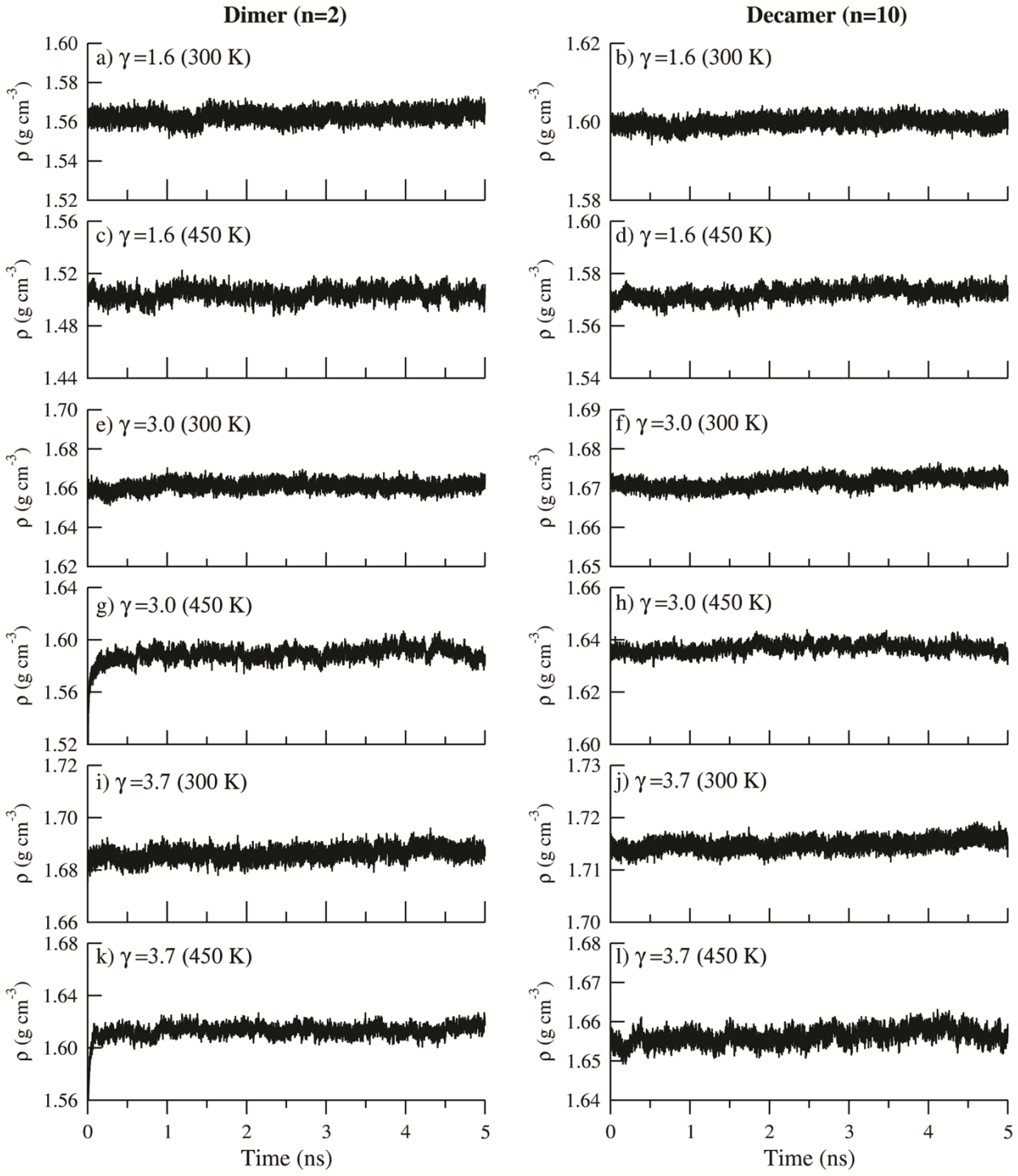


Figure S1: Density of PA doped ABPBI membrane for dimer and decamer from last 5 ns of equilibration at a-d) γ=1.6, e-h) γ=3.0 and i-l) γ=3.7.

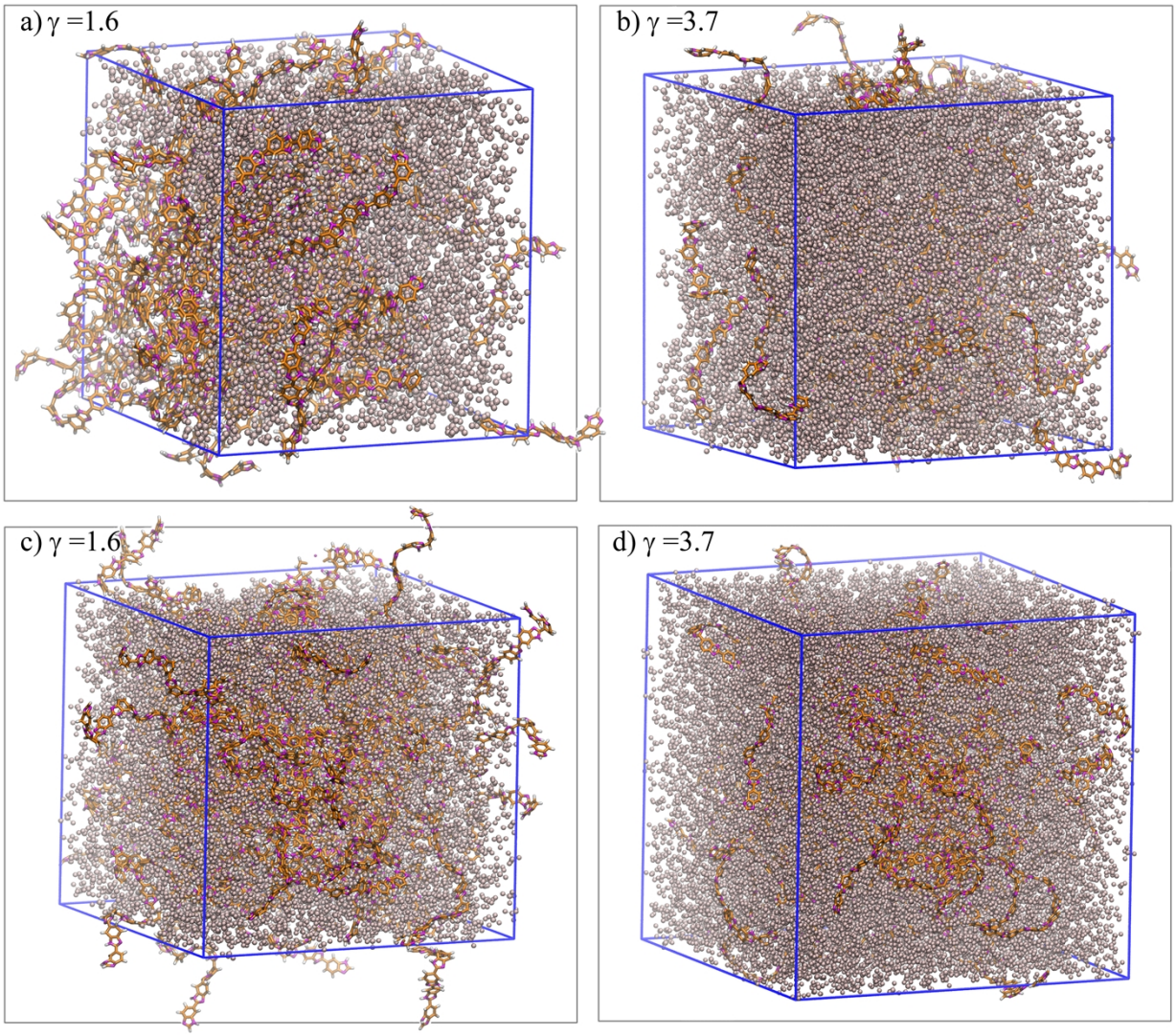


Figure S2: Snapshots of PA doped ABPBI membrane at 300 K from production run (a, b) for pentamer and (c, d) for decamer at γ =1.6 and γ =3.7 respectively. [ABPBI membrane=Licorice and PA molecule=CPK (Hydrogen atoms were not displayed)]

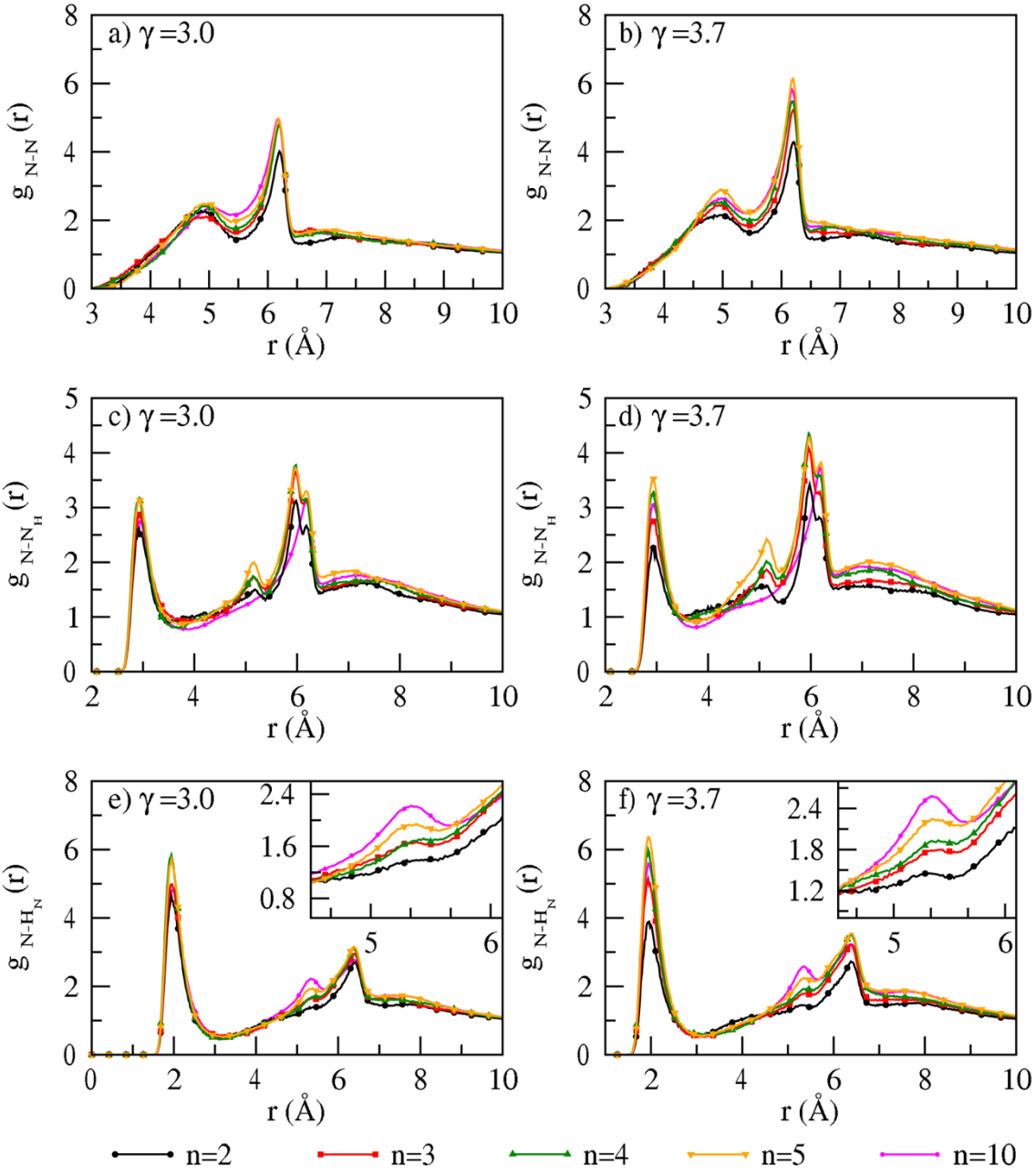


Figure S3: RDFs from (a,b) N-N, (c,d) N-N_H and (e,f) N-H_N interactions at T = 300 K and γ = 3.0 and 3.7.

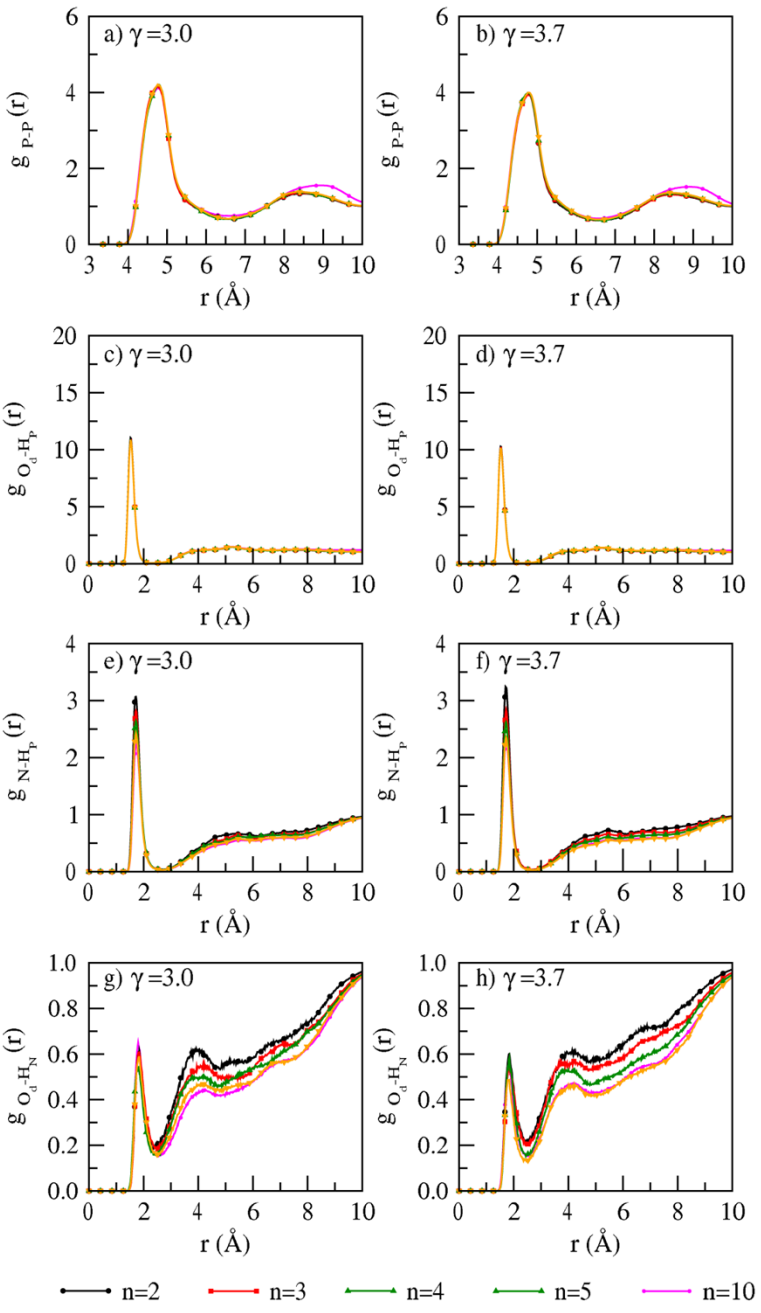


Figure S4: RDFs from (a,b) P-P, (c,d) O_d-H_p, (e,f) N-H_p, (g,h) O_d-H_N interactions at T = 300 K and γ = 3.0 and 3.7.

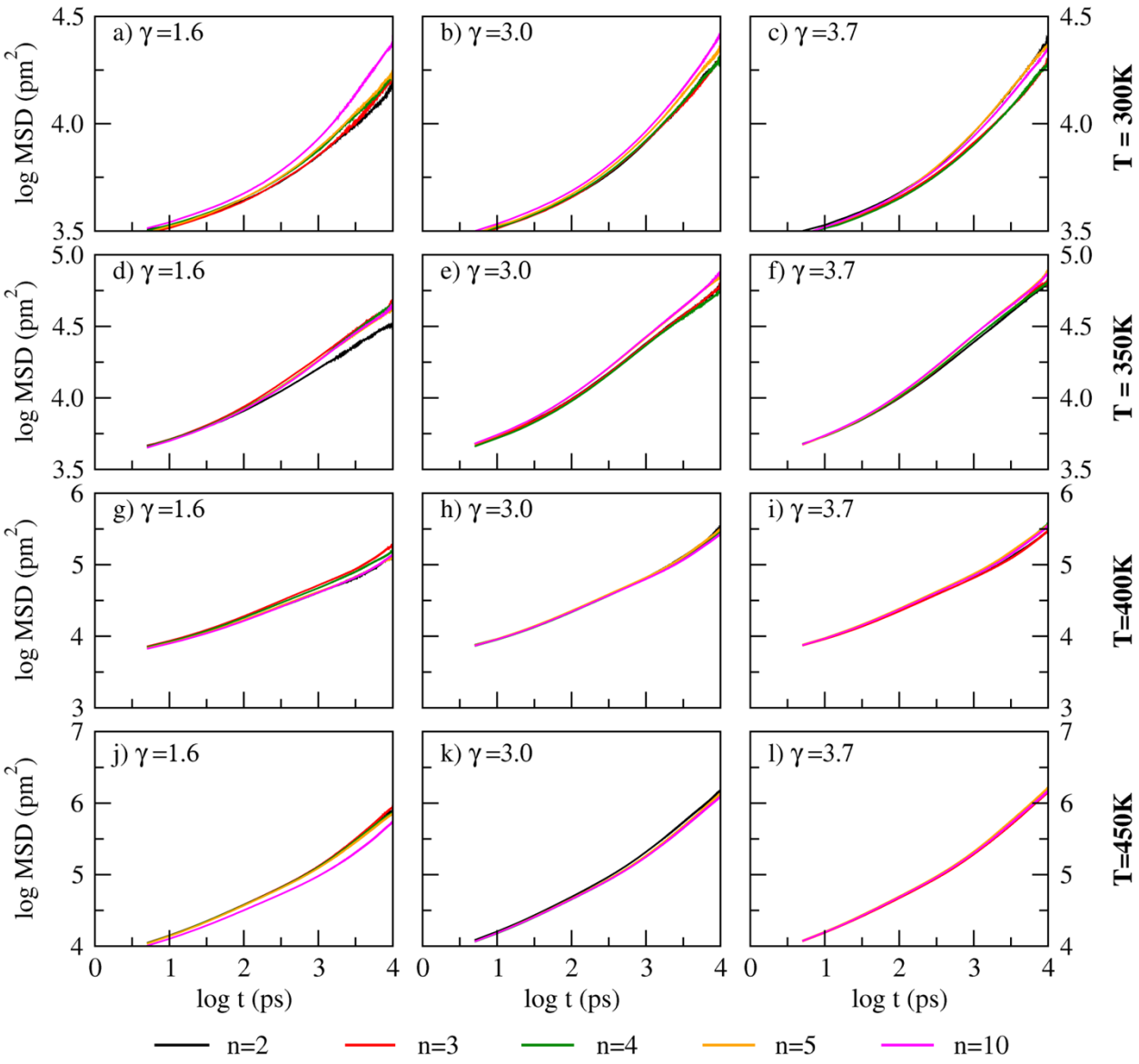


Figure S5: Mean Square Displacement of PA at a-c) 300 K, d-f) 350 K, g-i) 400 K and j-l) 450 K.

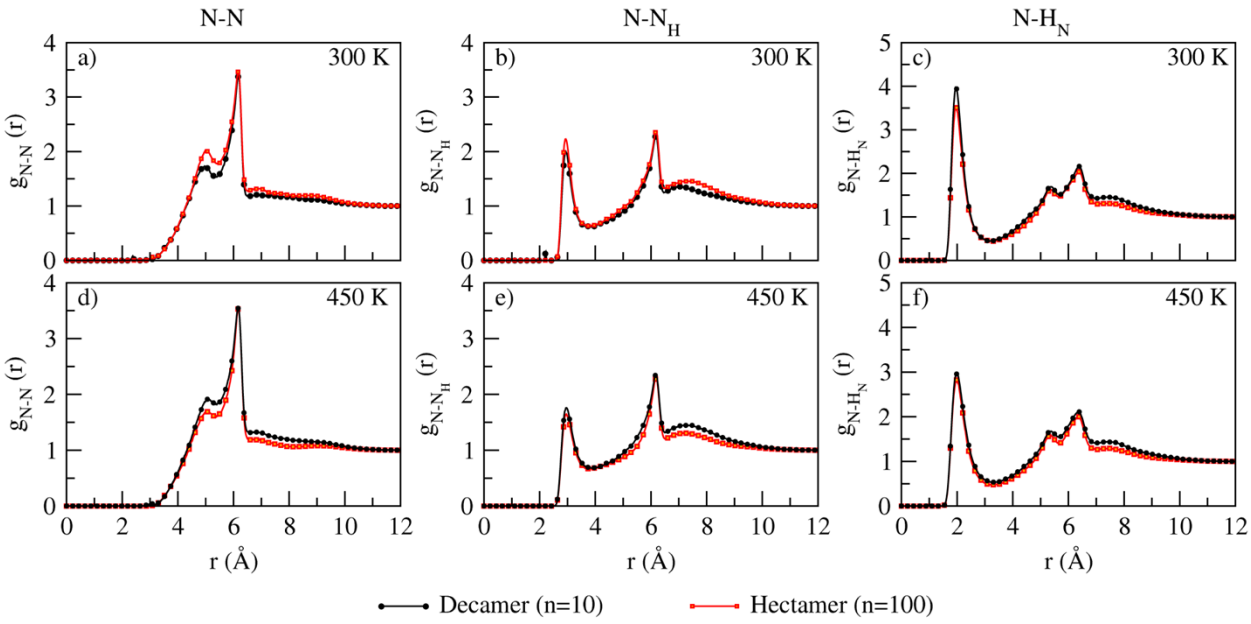


Figure S6: RDFs of imidazole interactions (N-N, N-N_H and N-H_N) at a-c) 300 K and d-f) 450 K for Decamer and Hectamer respectively.

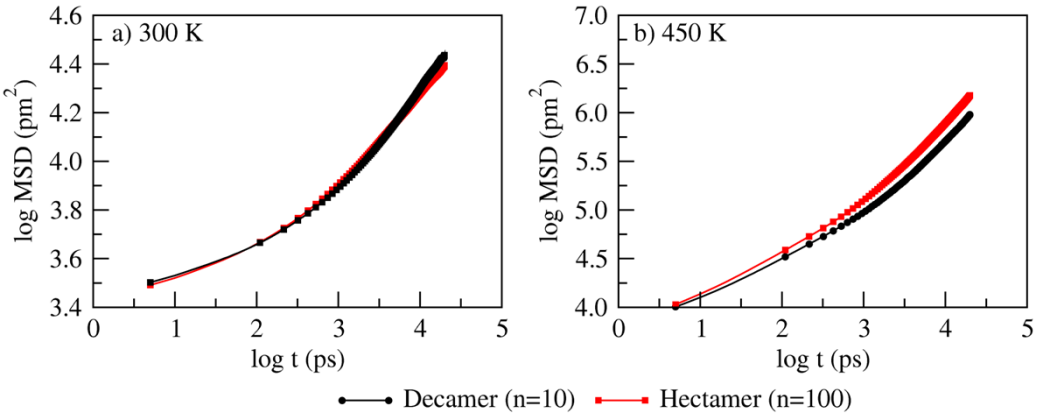


Figure S7: Mean Square Displacement of PA at a) 300 K and b) 450 K for Decamer and Hectamer respectively.