Supporting Information
for
A Molecular Dynamics Study on Adsorption Mechanisms of Polar, Cationic, and Anionic Polymers on Montmorillonite

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1. Molecular models of four polymers

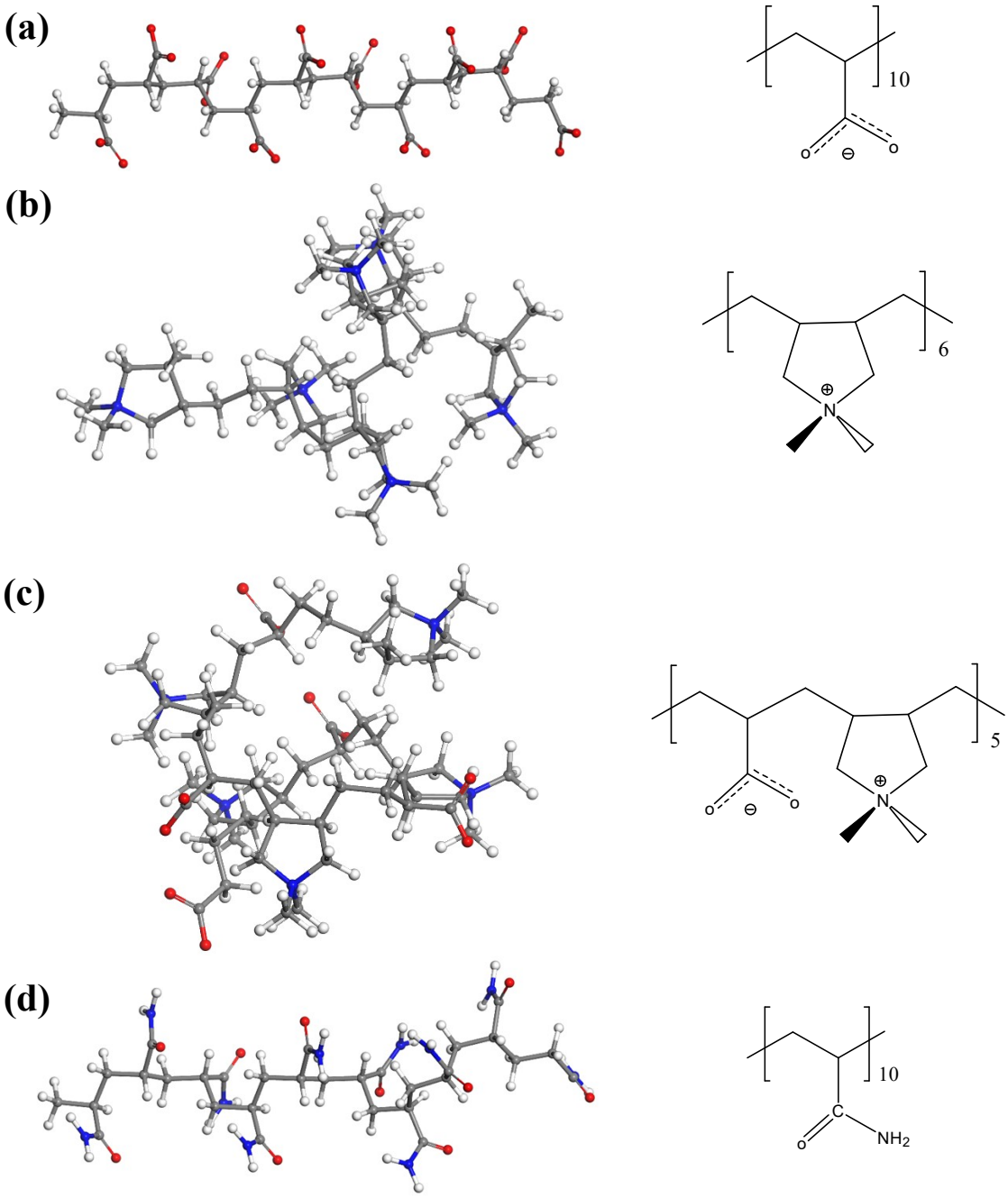
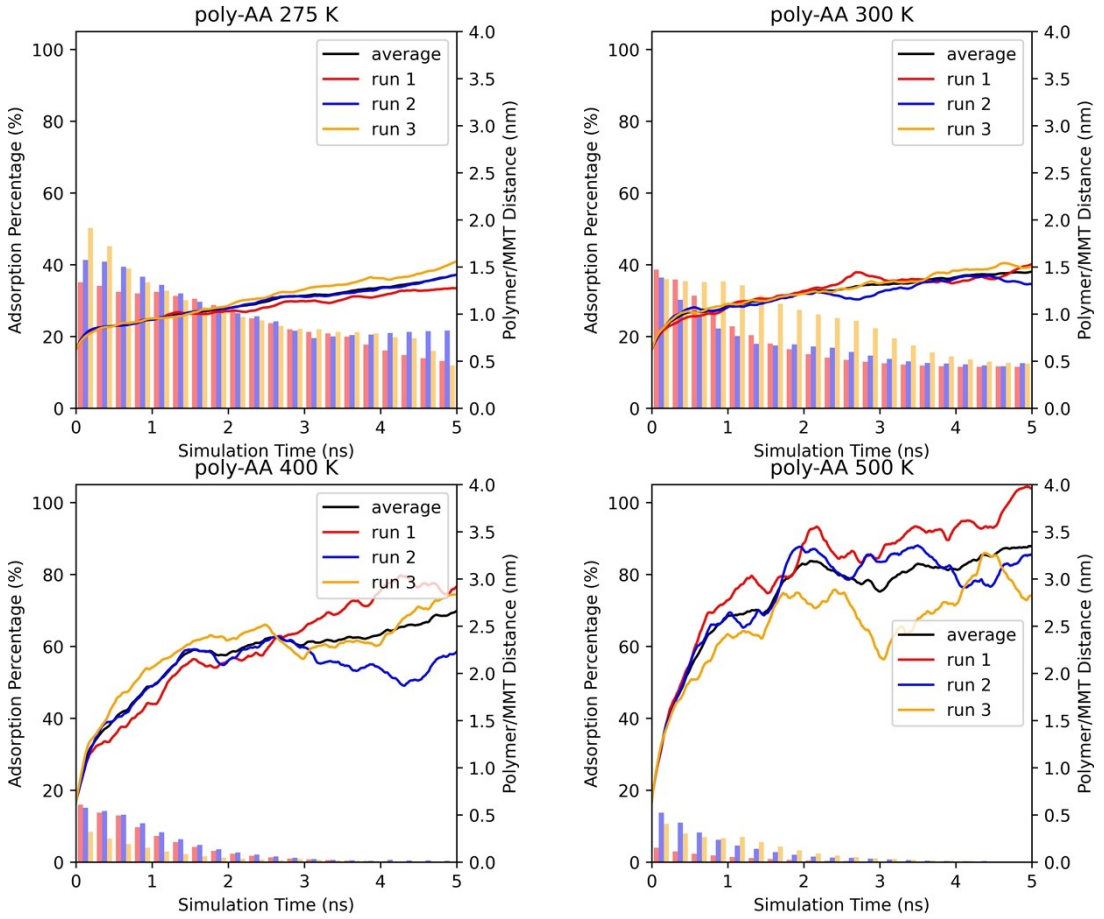


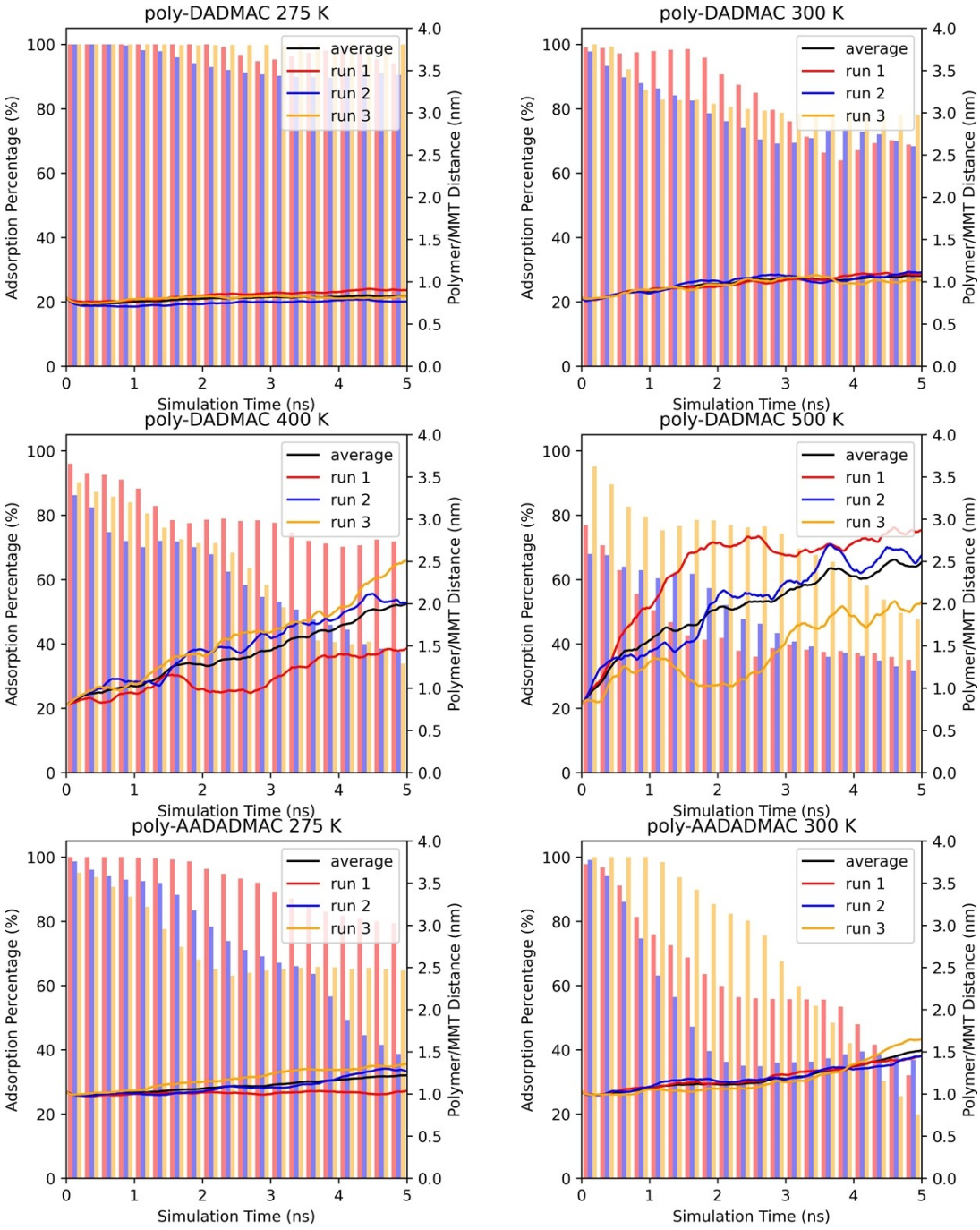
Figure S1. Structures of (a) poly-AA, (b) poly-DADMAC, (c) poly-AADADMAC, and (d) poly-AM chains. Red, gray, white, and blue represent O, C, H, and N atoms, respectively. For charged polymers poly-AA and poly-DADMAC, counter ions K^+ and Cl^- are not shown in this figure but are added to the salt solutions to make the systems charge-neutral.

2. Effects of temperatures

Figure S2 shows the desorption behaviors of four polymers at different temperatures (275K, 300K, 400K, and 500K). This figure is intended to supplement Figure 2 in the main manuscript by providing the results of three separate MD runs under each simulation condition.

Table S1 lists the D_s of K^+, Cl^-, polymer chains, and water under different temperatures. This table is intended to supplement Table 2 in the main manuscript. It is evident that D_s of K^+, Cl^-, and water are similar under the same temperature no matter which polymer is present. However, the D_s values of polymer chains are rather different with stronger adsorbed chains having smaller D_s values.




poly-DADMAC 275 K
poly-DADMAC 300 K
poly-DADMAC 400 K
poly-DADMAC 500 K
poly-AADADMAC 275 K
poly-AADADMAC 300 K
average
run 1
run 2
run 3
Adsorption Percentage (%)
Polymer/MMT Distance (nm)
Simulation Time (ns)

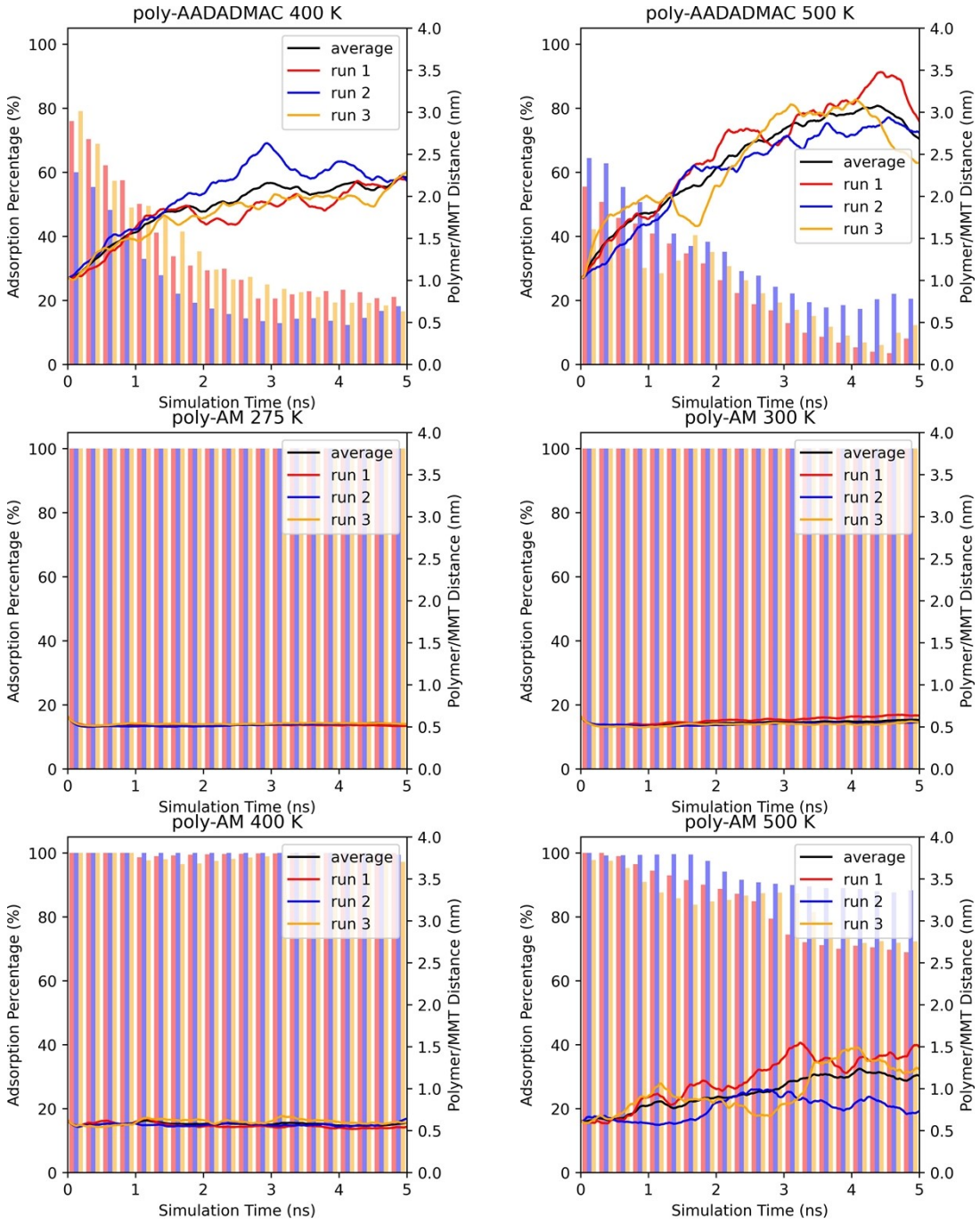


Figure S2. The polymer/MMT distances (curves, axis on the right) and the ratios of adsorbed polymer chains (bars, axis on the left) of four polymers at 275 K, 300 K, 400 K, and 500 K (16 cases). All simulations in this figure were performed with a 10 KCl wt% salt concentration and at 50 MPa pressure.

Table S1. The density of polymer/salt solution and D_s of K^+, Cl^-, polymers chains, and water under different temperatures.*

Polymer	T (K)	Density (g/cm^3)	D_s (10^{-9} m^2/s)			
			K^+	Cl^-	polymer chains	water
poly-AA	275	1.1208	0.3111	0.3066	0.0527	0.4899
poly-DADMAC	275	1.0971	0.3122	0.2764	0.0158	0.4739
poly-AADADMAC	275	1.0976	0.3228	0.3004	0.0377	0.5064
poly-AM	275	1.1000	0.3464	0.3355	0.0091	0.519
poly-AA	300	1.1093	0.542	0.5829	0.1014	0.9099
poly-DADMAC	300	1.0856	0.5995	0.5493	0.0513	0.9261
poly-AADADMAC	300	1.0863	0.5317	0.5455	0.0615	0.9397
poly-AM	300	1.0891	0.5773	0.5323	0.0233	0.9754
poly-AA	400	1.0388	2.4737	2.6243	0.5059	4.5685
poly-DADMAC	400	1.0183	1.9866	2.3571	0.4728	4.418
poly-AADADMAC	400	1.0175	2.0013	2.4568	0.4678	4.4786
poly-AM	400	1.0210	2.5375	2.8007	0.1264	4.7123
poly-AA	500	0.9377	5.5131	6.8107	2.4269	11.3472
poly-DADMAC	500	0.9192	5.5412	6.5436	1.2065	11.1709
poly-AADADMAC	500	0.9201	5.085	6.0492	0.8268	10.9178
poly-AM	500	0.9210	5.1615	6.0597	0.9311	11.0687

* All simulations in this table are at 50 MPa and with 10 wt% KCl.

3. Effects of pressures

Table S2. The density of polymer/salt solution and D_s of K^+, Cl^-, polymers chains, and water under different pressures.*

Polymer	P (MPa)	Density (g/cm^3)	D_s (10^{-9} m^2/s)			
			K^+	Cl^-	polymer chains	water
poly-AA	20	1.0243	2.5389	2.6277	0.6325	4.6898
poly-AA	50	1.0388	2.4737	2.6243	0.5059	4.5685
poly-AA	200	1.0961	2.1033	2.3932	0.4014	3.9778
poly-DADMAC	20	1.0026	2.9239	3.3362	0.5737	5.1414
poly-DADMAC	50	1.0183	1.9866	2.3571	0.4728	4.4180
poly-DADMAC	200	1.0742	1.8962	2.4684	0.4382	3.9851
poly-AADADMAC	20	1.0036	1.9613	2.5227	0.5182	4.6086
poly-AADADMAC	50	1.0175	2.0013	2.4568	0.4678	4.4786
poly-AADADMAC	200	1.0741	1.5651	2.3218	0.5069	3.9729
poly-AM	20	1.0062	2.7822	2.9009	0.2010	5.0242
poly-AM	50	1.0210	2.5375	2.8007	0.1264	4.7123
poly-AM	200	1.0790	2.5489	2.5797	0.1563	4.2885

* All simulations in this table are at 400 K and with 10 wt% KCl.

4. Effects of salinity

Figure 4 in the main manuscript demonstrates the desorption behaviors of polymers at 500 K. As a comparison, Figure S3 below shows the results at 275 K.

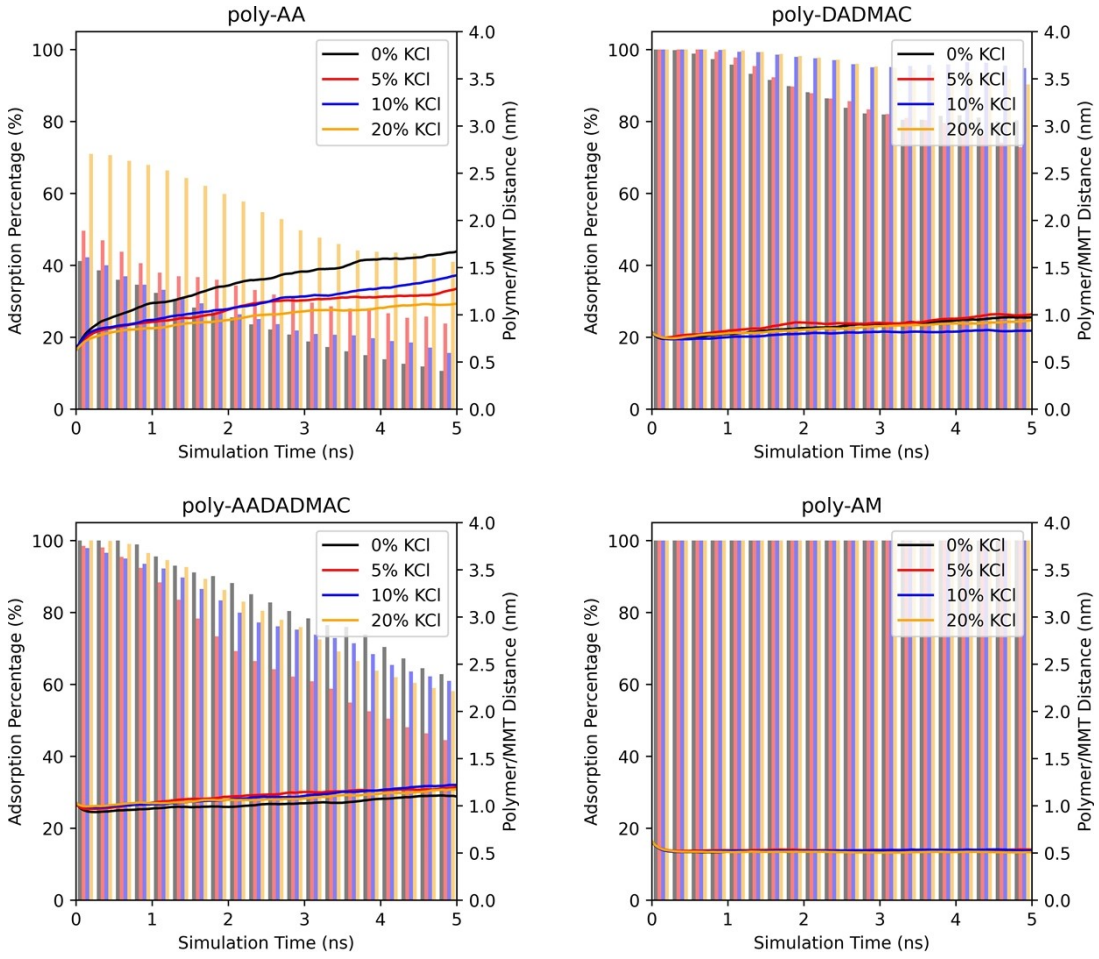


Figure S3. The polymer/MMT distances (curves, axis on the right) and the ratios of adsorbed polymer chains (bars, axis on the left) of four polymers under different KCl concentrations. All simulations in this figure were performed at 275 K and 50 MPa pressure.

Table S3. D_s of K^+, Cl^-, polymers chains, and water under different KCl concentrations and temperatures.[a]

Polymer	T (K)	KCl[b] (wt %)	D_s (10^{-9} m^2/s)			
			K^+	Cl^-	polymer chains	water
poly-AA	275	0	0.2975	-	0.0691	0.5039
poly-AA	275	5	0.3197	0.3084	0.0464	0.5006
poly-AA	275	10	0.3111	0.3066	0.0527	0.4899
poly-AA	275	20	0.2527	0.2519	0.0233	0.4291
poly-DADMAC	275	0	-	0.2789	0.0287	0.514
poly-DADMAC	275	5	0.3154	0.2977	0.0256	0.5089
poly-DADMAC	275	10	0.3122	0.2764	0.0158	0.4739
poly-DADMAC	275	20	0.2745	0.2536	0.0218	0.4361
poly-AADADMAC	275	0	-	-	0.0256	0.5140
poly-AADADMAC	275	5	0.3014	0.3157	0.0219	0.5066
poly-AADADMAC	275	10	0.3228	0.3004	0.0377	0.5064
poly-AADADMAC	275	20	0.2464	0.2395	0.0232	0.4559
poly-AM	275	0	-	-	0.0083	0.5525
poly-AM	275	5	0.3321	0.3141	0.0058	0.5373
poly-AM	275	10	0.3464	0.3355	0.0091	0.5190
poly-AM	275	20	0.2939	0.2783	0.0053	0.4694
poly-AA	500	0	5.0164	-	3.0270	13.3395
poly-AA	500	5	4.7940	6.1801	1.0897	11.4852
poly-AA	500	10	5.5131	6.8107	2.4269	11.3472
poly-AA	500	20	4.3849	4.9149	1.3108	9.3031
poly-DADMAC	500	0	-	5.9761	1.0113	12.2470
poly-DADMAC	500	5	4.8620	6.6595	1.3979	11.8455
poly-DADMAC	500	10	5.5412	6.5436	1.2065	11.1709
poly-DADMAC	500	20	4.5734	5.0952	0.8976	9.4739
poly-AADADMAC	500	0	-	-	2.2570	13.2665
poly-AADADMAC	500	5	5.2066	6.4398	1.5864	11.9313
poly-AADADMAC	500	10	5.0850	6.0492	0.8268	10.9178
poly-AADADMAC	500	20	4.3857	5.0773	1.2199	9.3176
poly-AM	500	0	-	-	1.1394	12.3378
poly-AM	500	5	3.9280	7.4439	0.9045	11.6958
poly-AM	500	10	5.1615	6.0597	0.9311	11.0687
poly-AM	500	20	4.4523	4.8448	0.5926	9.5864

[a] All simulations in this table are at 50 MPa.

[b] In cases where the concentration of KCl equals 0%, there are still K^+ ions in poly-AA solutions and Cl^- ions in poly-DADMAC solutions to counter the negative and positive charges carried by the polymer chains, respectively. In these cases, either Cl^- or K^+ is absent from the system, and their D_s are shown as '-' in the table.

5. Effects of salt types

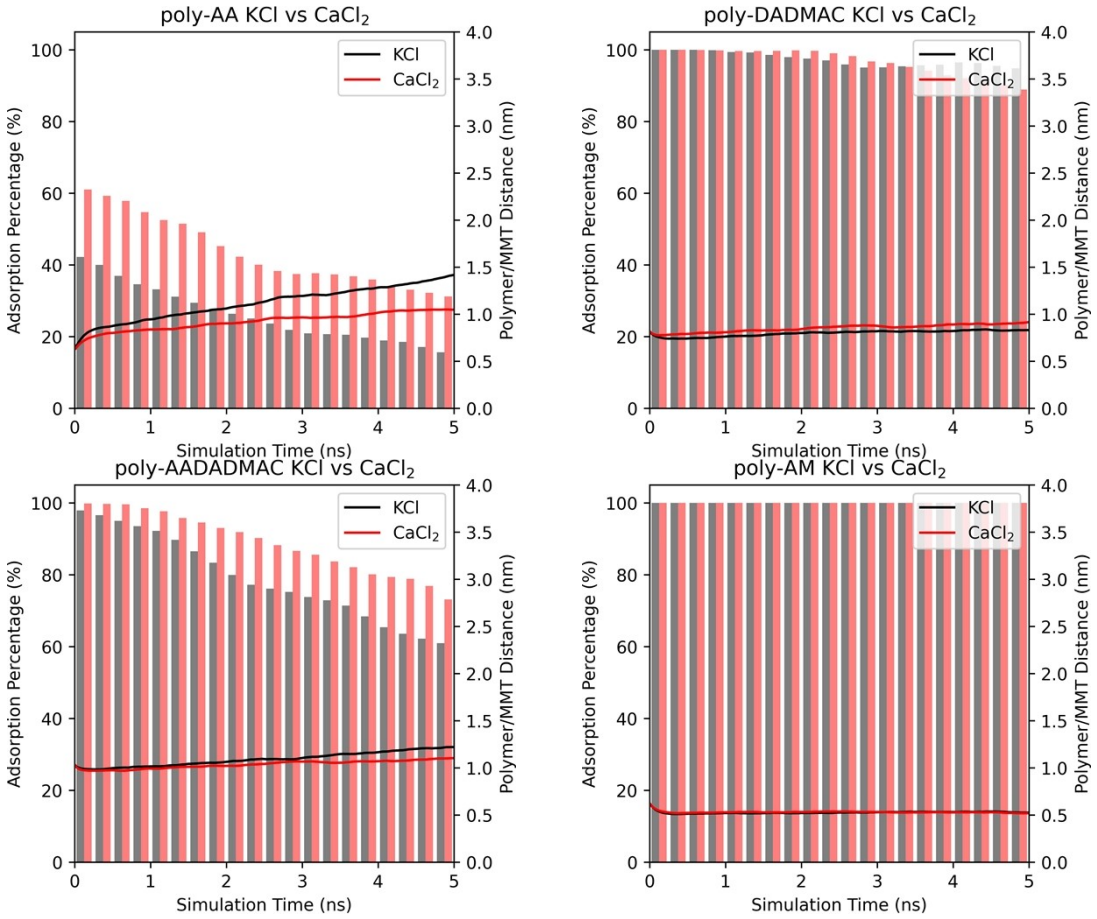


Figure S4. The polymer/MMT distances and the ratios of adsorbed polymer chains of four polymers as functions of MD simulation time in 10 wt% KCl and 7.54 wt% $CaCl_2$ solutions at 275 K and 50 MPa.

Table S4. D_s of cations, Cl^-, polymers chains, and water in KCl or $CaCl_2$ solutions.[a]

Polymer	T (K)	Salt[b]	D_s (10^{-9} m^2/s)			
			K^+ or Ca^{2+}	Cl^-	polymer chains	water
poly-AA	275	KCl	0.3111	0.3066	0.0527	0.4899
poly-AA	275	$CaCl_2$	0.1297	0.2224	0.0189	0.3804
poly-DADMAC	275	KCl	0.3122	0.2764	0.0158	0.4739
poly-DADMAC	275	$CaCl_2$	0.1035	0.2306	0.022	0.386
poly-AADADMAC	275	KCl	0.3228	0.3004	0.0377	0.5064
poly-AADADMAC	275	$CaCl_2$	0.0872	0.2277	0.0193	0.3844
poly-AM	275	KCl	0.3464	0.3355	0.0091	0.519
poly-AM	275	$CaCl_2$	0.1053	0.2269	0.0067	0.3965
poly-AA	500	KCl	5.5131	6.8107	2.4269	11.3472
poly-AA	500	$CaCl_2$	2.9594	4.8637	1.331	10.3893
poly-DADMAC	500	KCl	5.5412	6.5436	1.2065	11.1709
poly-DADMAC	500	$CaCl_2$	2.533	4.8374	0.877	9.9246
poly-AADADMAC	500	KCl	5.085	6.0492	0.8268	10.9178
poly-AADADMAC	500	$CaCl_2$	2.6273	6.0456	1.3196	10.631
poly-AM	500	KCl	5.1615	6.0597	0.9311	11.0687
poly-AM	500	$CaCl_2$	2.7439	4.9962	0.5305	10.3349

[a] All simulations in this table are at 50 MPa.

[b] Salt concentrations are 10 wt% for KCl and 7.54 wt% $CaCl_2$, respectively.

6. Adsorption mechanisms at 275 K

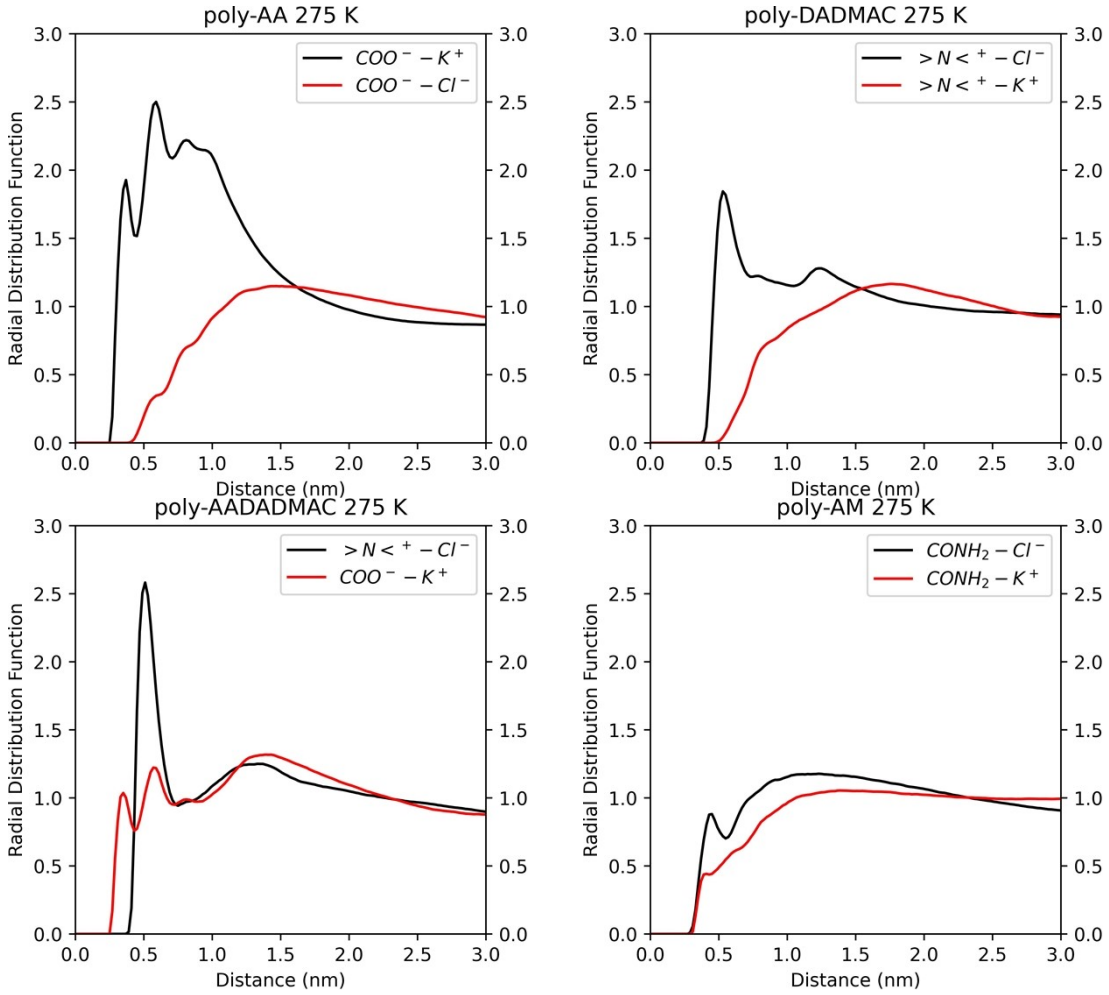


Figure S5. The radial distribution functions (RDFs) of four polymers adsorbed on MMT at 275 K, 50 MPa, in 10 wt% KCl solutions.

7. Desorption under high temperatures

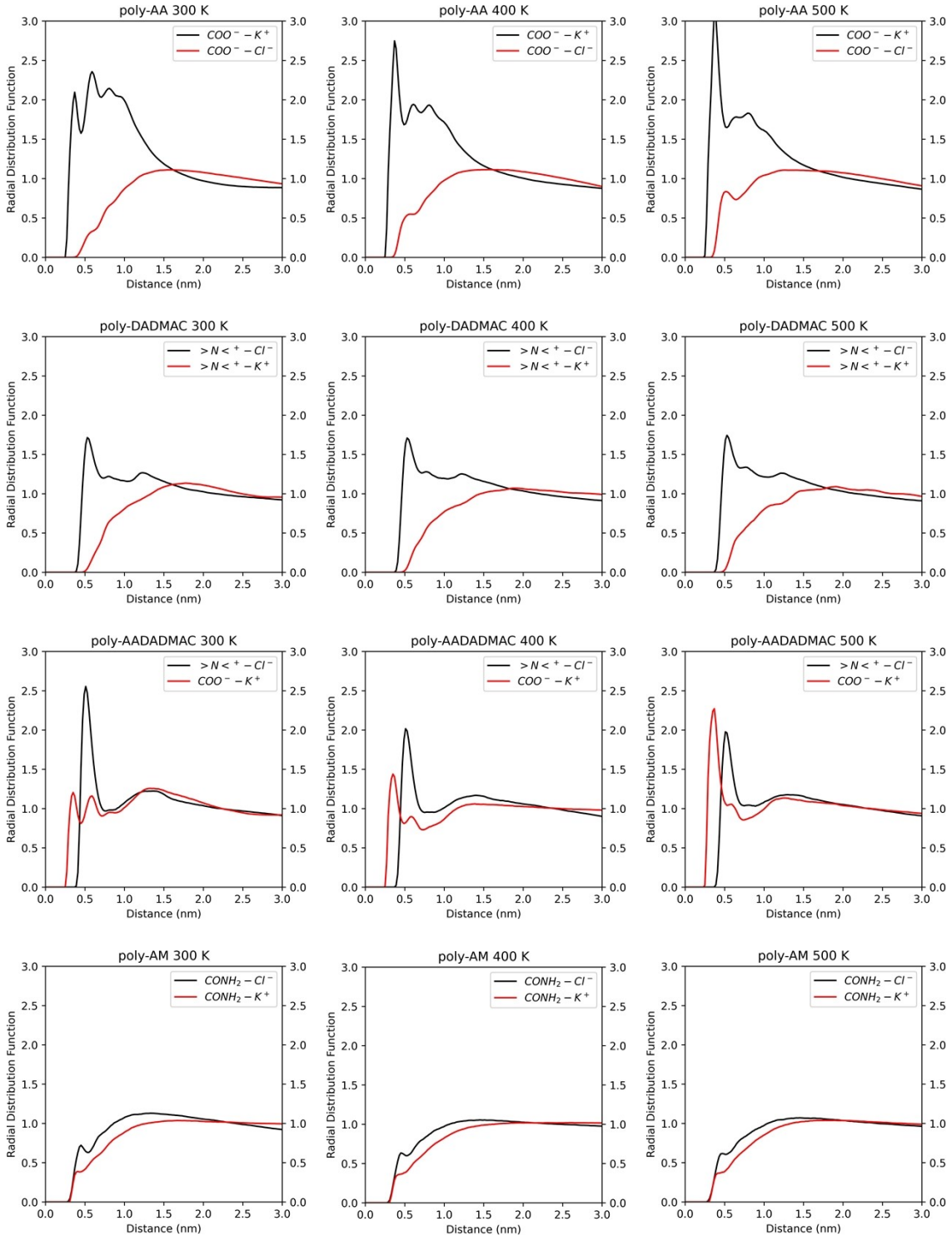


Figure S6. RDF of four polymers adsorbed on MMT at 300 K, 400 K, and 500 K.

All simulations in this figure are at 50 MPa, in 10 wt% KCl solutions.