Supplementary information

Growth of membranes formed by associating polymers at interfaces

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Data on titration of poly(methacrylic acid) (PMAA) solution with NaOH solution

The dependence of the PMAA ionization degree α on pH (Fig. 6) was determined by using the potentiometric titration data as

$$\alpha = \frac{c_{\mathrm{NaOH}} + c_{\mathrm{H^+}}}{c_{\mathrm{MAA}}},$$

where c_{NaOH} and $c_{\mathrm{H^+}}$ are the molarities of added NaOH and free hydrogen ions, respectively, and c_{MAA} is the molarity of monomer units.

For an initial PMAA solution in water with 1 wt % polymer concentration, the molarity is $c_{\mathrm{MAA(0)}} = 0.01\,\rho_{\mathrm{w}}/\mu_{\mathrm{MMA}} \approx 0.116\ \mathrm{mol/L}$ (N_{A} is the Avogadro number, ρ_{w} is the water density, $\mu_{\mathrm{MMA}} = 86\ \mathrm{g/mol}$ is the molar mass of monomer unit). The molarity of the NaOH solution is $c_{\mathrm{NaOH(0)}} = 0.192\ \mathrm{mol/L}$. The volume of NaOH solution added is V_{add}. The molarity of H^+ ions in the polymer solution is calculated as $c_{\mathrm{H^+}} = 10^{-\mathrm{pH}}$. The total volume of the polymer solution $V_{\mathrm{tot}} = V_0 + V_{\mathrm{add}}$, where $V_0 = 9.3\ \mathrm{ml}$ is the initial volume. The molarity of NaOH ions in the polymer solution is calculated as $c_{\mathrm{NaOH}} = c_{\mathrm{NaOH(0)}}\,V_{\mathrm{add}}/V_{\mathrm{tot}}$. The polymer molarity is calculated as $c_{\mathrm{MAA}} = c_{\mathrm{MAA(0)}}\,V_0/V_{\mathrm{tot}}$.

V_{add}, ml	pH	$c_{\mathrm{H^+}}$, mol/L	V_{tot}, ml	c_{NaOH}, mol/L	c_{MAA}, mol/L	α
0	2,86	0,00138	9,3	0	0,1163	0,0119
0,105	3,29	0,000513	9,405	0,0021	0,1150	0,0231
0,205	3,8	0,000158	9,505	0,0041	0,1138	0,0378
0,305	4,22	6,03E-05	9,605	0,0061	0,1126	0,0547
0,355	4,3	5,01E-05	9,655	0,0071	0,1120	0,0635
0,405	4,45	3,55E-05	9,705	0,0080	0,1114	0,0722
0,455	4,64	2,29E-05	9,755	0,0090	0,1109	0,0810
0,505	4,76	1,74E-05	9,805	0,0099	0,1103	0,0898
0,555	4,9	1,26E-05	9,855	0,0108	0,1097	0,0986
0,605	5,05	8,91E-06	9,905	0,0117	0,1092	0,1075
0,655	5,08	8,32E-06	9,955	0,0126	0,1086	0,1163
0,755	5,23	5,89E-06	10,055	0,0144	0,1075	0,1341
0,805	5,25	5,62E-06	10,105	0,0153	0,1070	0,1429
0,855	5,29	5,13E-06	10,155	0,0162	0,1065	0,1518
1,005	5,41	3,89E-06	10,305	0,0187	0,1049	0,1784
1,105	5,42	3,8E-06	10,405	0,0204	0,1039	0,1962
1,205	5,52	3,02E-06	10,505	0,0220	0,1029	0,2139
1,305	5,57	2,69E-06	10,605	0,0236	0,1020	0,2316
1,505	5,7	2E-06	10,805	0,0267	0,1001	0,2671
1,705	5,7	2E-06	11,005	0,0297	0,0983	0,3026
2,205	6,1	7,94E-07	11,505	0,0368	0,0940	0,3914

2,705	6,45	3,55E-07	12,005	0,0432	0,0901	0,4801
3,205	6,8	1,58E-07	12,505	0,0492	0,0865	0,5688
3,705	7,4	3,98E-08	13,005	0,0547	0,0832	0,6576

Experimental data on membrane growth for different pH

These data were obtained by *in situ* thickness measurements with a reflected light microscope mounted with an optical spectrometer (specim V8 connected to a camera). We focus white light on the oil-water interface. The spectrometer provides the reflected intensity as a function of wave length from which we deduce the membrane thickness (Fig. 7). The index of refraction 1.4 is used in the calculations.

pH=3

t, min	*h*, µm	error, µm
70	0,36	0,05
90	0,4	0,05
120	0,47	0,05
190	0,54	0,05
270	0,645	0,1
530	0,87	0,1
860	1,1	0,1
1130	1,27	0,1
1200	1,3	0,1
1330	1,375	0,1
1530	1,47	0,1
1730	1,56	0,1
1930	1,63	0,1
2130	1,705	0,1
2330	1,78	0,1

pH=4.5

t, min	*h*, µm	error, µm
50	0,26	0,02
100	0,385	0,02
200	0,48	0,025
250	0,545	0,05
350	0,61	0,05
480	0,74	0,05
680	0,86	0,05
810	0,96	0,05
1060	1,09	0,1
1500	1,3	0,1
2100	1,53	0,1
2800	1,74	0,1
3700	1,955	0,1
4300	2,09	0,2
5200	2,24	0,2
5900	2,34	0,2
6500	2,435	0,2
7400	2,55	0,2

pH=4.9

t, min	*h*, µm	error, µm
150	0,21	0,02
440	0,29	0,02
600	0,38	0,025
880	0,4	0,05
1340	0,49	0,05
2040	0,58	0,05
4440	0,77	0,05
5740	0,81	0,05
9640	0,9	0,1
11940	0,95	0,1
13840	0,98	0,1
15540	1	0,1
18240	1,05	0,1

pH=5

t, min	*h*, µm	error, µm
150	0,21	0,02
440	0,29	0,02
600	0,38	0,025
880	0,4	0,05
1340	0,49	0,05
2040	0,58	0,05
4440	0,77	0,05
5740	0,81	0,05
9640	0,9	0,1
11940	0,95	0,1
13840	0,98	0,1
15540	1	0,1
18240	1,05	0,1

pH=5.1

t, min	*h*, µm	error, µm
2400	0,39	0,025
4500	0,48	0,05
6200	0,54	0,05
10000	0,58	0,05