

Wettability change of Diamine Polymer Coating via CO₂ capture

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1. Introduction

Superhydrophilic surface based on zwitterion (e.g., sulfobetaine or phosphorylcholine) polymers has been proposed as anti-fouling or self-cleaning surface. Takahara, et al., investigated superhydrophilic zwitterion polymer brushes and their detailed hydration status of polymer-water interfaces by neutron reflectivity (Takahara, et al., *Polym. J.*, **2016**, *48*, 325–331; *Polymer*, **2016**, *98*, 464-469). Compared to such intrinsic zwitterion polymers, we designed *diamine containing pre-polymers* to accumulate CO₂ at water interface to form zwitterion (Scheme 1), which induced significant wettability change by just immersion in water under open-air conditions (low CO₂ conc. of 300 ppm). NMR, IR, and contact angle measurements verified CO₂ capture by diamine polymer **P1** and **P4**, but not by **P2** and **P3**. Further understanding and better material design of such environmentally adaptive coating, it is crucial to track the formation process of zwitterion and swelling behavior at polymer/water interface. The goal of this research is to estimate superhydrophilic layer thickness formed by CO₂ addition. NR was utilized to analyze deuterated water (D₂O) uptake and swelling behavior at interface comparing before and after CO₂ treatment. Time-slicing measurement of D₂O uptake can also monitor CO₂ responsive behavior of the diamine polymer coating.

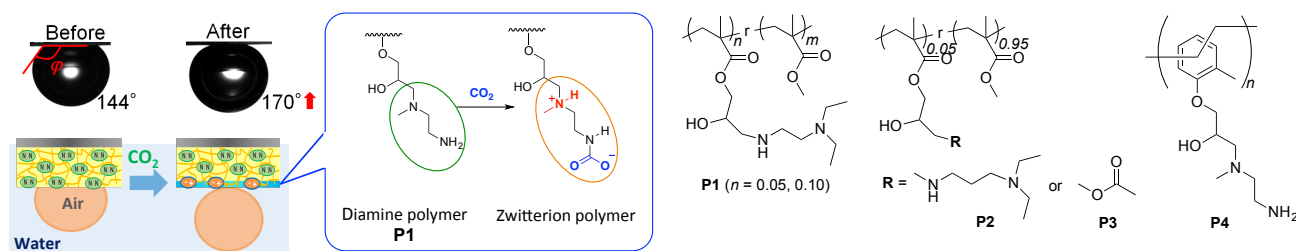


Fig. 1 CO₂ addition to the diamine polymer coating for superhydrophilic surface formation.

2. Experiment

Diamine polymers **P1** (diamine content = 5, 10 mol%) were synthesized and spin-coated from 1-methoxypropanol solution onto quartz substrate (5 x 5 cm). The control samples **P2** and **P3** were also prepared. The crosslinked epoxy coating was also prepared using **P4** by thermal curing for 3 h. The target thickness of the coating is 100 nm. Two solvent conditions are employed for NR experiments: a) D₂O degassed and treated with argon bubble (CO₂ free condition), and b) D₂O with CO₂ bubbling for 15 min (saturated CO₂ condition, 3 x 10⁻² mol/L). The coating was set in the special liquid cell, and immersed in two solvent conditions. The first experiment (A) is to check swelling behavior of the coatings with different composition at equilibrium state. The sample layer was quite thin (100 nm), so immersion time was set to 1 h for each experiment. To cover the q range from 0.08 to 2 nm⁻¹, the incident angle of neutrons is set at 0.3, 0.75, and 1.6°, and the reflectivity data was collected. The data analysis was performed using Motofit, assuming the monolayer model. Change in thickness, surface roughness, depth profile of D₂O provided the contribution of zwitterion formation, comparing conditions a) and b). After the first screening experiment, the optimized composition was determined. The second experiment (B, time-slicing NR measurement) was carried out for the crosslinked polymer coating **P4** (20 wt%) using special liquid cell with auto injector. D₂O was set under open air condition for 24 h and saturated with air (CO₂ conc. ~ 1.2 x 10⁻⁵ mol/L). The SLD change due to D₂O uptake was monitored over time (~3 h), and the profiles were analyzed every 10 min. All experiment was performed at 293 K.

3. Results

3.1 Swelling Behavior of Diamine Polymer Coating at Equilibrium State

NR profiles of the prepared polymer coating **P1-4** were measured and fitted by the monolayer model at different conditions: (a) under air, (b) immersed in D₂O saturated with argon, and (c) immersed in D₂O saturated with CO₂. Figure 2 shows the additional swelling of **P1** (diamine content 10mol%) at condition (c), ascribed to the zwitterion formation by CO₂ capture. Compared with **P1**, the control samples **P2** (with propylene spacer) and **P3** (acetate) did not show significant change in swelling behavior, which suggested the slight structural change around diamine moieties critically affected the CO₂ binding affinity (Table 1). These results corresponded well with our previous findings on NMR, IR and cross-sectional SIMS analyses.

Table 1 Thickness and SLD profile change of the coating by immersion in D₂O

Polymer	Condition	Thickness (nm)	Thickness ratio (%)	Roughness (nm)		SLD	D ₂ O ratio
				Polymer	Glass		
P1 (5 mol%)	Air	76.4	100	2.0	-	0.96	-
	Ar	79.7	104	8.3	5.9	1.7	0.14
	CO ₂	82.0	107	2.5	-	1.9	0.18
P1 (10 mol%)	Air	64.4	100	2.3	-	0.94	-
	Ar	69.6	108	1.4	6.0	1.9	0.18
	CO ₂	79.7	124	2.6	-	2.6	0.31
P2	Air	71.2	100	0.10	-	0.90	-
	Ar	74.0	104	1.2	1.0	1.5	0.11
	CO ₂	75.0	105	1.0	-	1.6	0.13
P3	Air	80.3	100	1.8	-	0.92	-
	Ar	83.1	103	1.0	0.94	1.4	0.087
	CO ₂	83.6	104	3.0	-	1.7	0.14
P4	Air	68.4	100	2.4	-	1.2	-
	Ar	71.6	105	5.6	2.0	2.6	0.28
	CO ₂	75.1	110	6.7	-	2.8	0.31

3.2 Time-Slicing Experiments for Swelling Behavior

Time-slicing NR experiments of the crosslinked polymer coating **P4** (120 and 180 nm) were carried out for 2 h using D₂O containing low conc. CO₂. As for 120 nm film, the swelling ratio reached at the constant value of 105% within 30 min, which clearly revealed this technique can track the dynamic change in swelling behavior at this time scale (Fig. 3). However, the swelling ratio after 700 min increased to be 108%, and Time-slicing experiments for longer time needs to be collected. As for 180 nm film, q range was not suitable to fit the data, and the swelling trend was not agreed with the data of 120 nm. Thickness dependence and the time scale to reach at equilibrium state will provide kinetics to describe the zwitterion layer formation.

4. Conclusion

Time-slicing NR technique is a powerful tool to monitor dynamic swelling behavior of CO₂-responsive polymer coating. Due to the beam time limitation, the time-slicing experiments were preliminary, but its applicability could be verified. Diamine polymer **P1** (10 mol%) would be more suitable for further investigation because of sufficient change in swelling ratio.

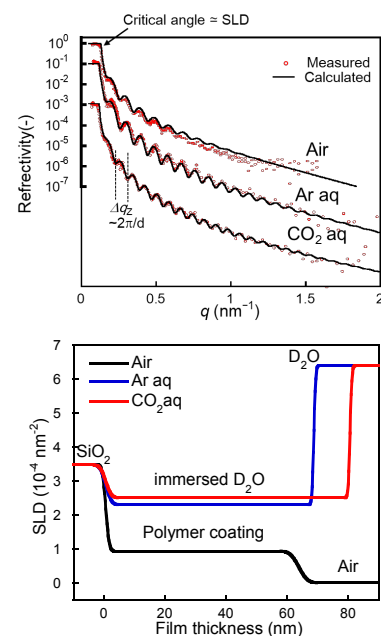


Fig. 2 (a) NR profile and fitting curve of **P1** (10mol%) film, and (b) SLD profile at equilibrium states.

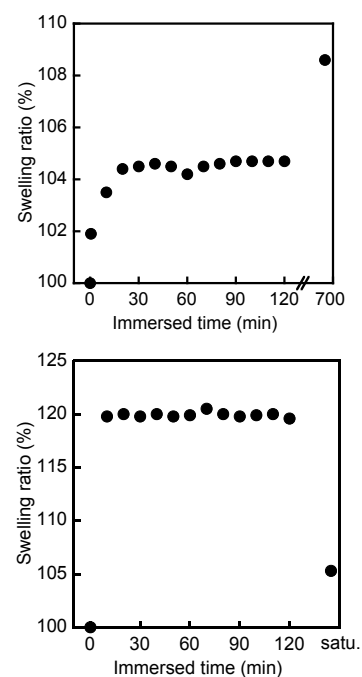


Fig. 3. Time-dependent swelling behavior of the crosslinked polymer coating **P4** (a) 120 nm, and (b) 180 nm.