Surface Modification of Parylene

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Introduction

Background:

Controlling surface wettability is important for microfluidic devices. Parylene is commonly used as a dielectric coating on lab-on-a-chip devices, but current methods for chemically modifying parylene can leave the surface rough and uneven. Our approach to modifying the wettability uses phenyl azides containing either a hydrophilic tail consisting of a pegylated (PEGA) phenyl azide or a hydrophobic tail consisting of a perfluorinated (PFA) phenyl azide. The parylene surface is coated with the phenyl azide and irradiated with UV light. Irradiation excites the azide to form a nitrene which then inserts into a carbon-hydrogen bond at the parylene surface.

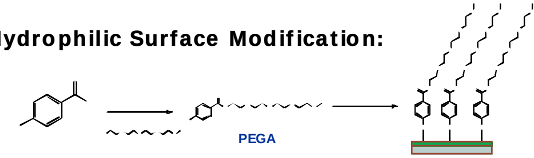
Advantages of lab-on-a-chip compared to conventional lab techniques:

- Lower reagent consumption
- Faster processing time
- Reduced waste

Goal: Find a convenient method for modifying and patterning parylene.

Experimental

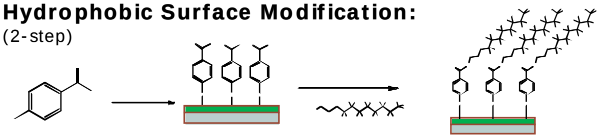
Hydrophilic Surface Modification:



PEGA (shown) was coated into the parylene surface and exposed to UV light (10 min, 10 cm from the light source) to produce the desired surface chemistry. The coated parylene surfaces were then rinsed and allowed to dry for 5 min before contact angle measurements were made. Parylene surfaces were modified with PFA (not shown), the hydrophobic analog of PEGA, in the same way. Controls were parylene surfaces treated exactly as the PEGA- and PFA-coated surfaces.

Hydrophobic Surface Modification:

(2-step)



Predicted Droplet Shape

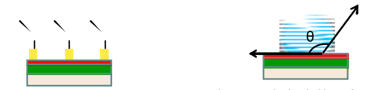


Figure 1. A hydrophobic surface normally exhibits a contact angle of >90˚.

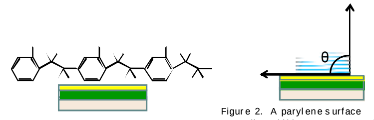


Figure 2. A parylene surface normally exhibits a contact angle of approximately 90˚.

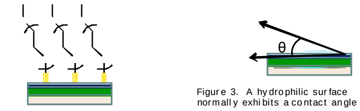
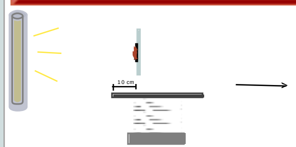


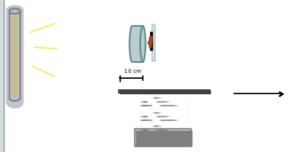
Figure 3. A hydrophobic surface normally exhibits a contact angle of < 80˚.

Results



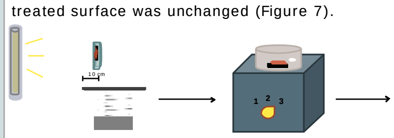
	Uncoated parylene		Coated parylene	
	Contact angle before irrad.	Contact angle after irrad.	Contact angle before irrad.	Contact angle after irrad.
PEGA	93˚	70˚ ± 5	90˚	58˚ ± 5
PFA	87˚	66˚ ± 4	90˚	95˚ ± 3

Experiment 1: UV treatment of PEGA- & PFA- coated parylene. UV light was used to modify a parylene-surfaced chip coated with either PEGA or PFA to produce the desired surface chemistry. A 100 µL solution of PEGA or PFA was deposited onto the parylene and dried at 60˚C. The coated parylene devices were then irradiated for 10 min at 10 cm distance from the light source. The water contact angle on *both the untreated and treated surfaces changed* after irradiation, which indicates that another process is happening other than PEGA or PFA adhering to the surface. These results suggest the possibility of using only irradiation to modify the surface wettability (Figure 5 and Experiment 2).



	Uncoated parylene		Coated parylene	
	Contact angle before irrad.	Contact angle after irrad.	Contact angle before irrad.	Contact angle after irrad.
PEGA	91˚	91˚ ± 2	90˚	74˚ ± 2
PFA	91˚	91˚ ± 2	84˚	89˚

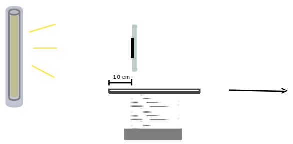
Experiment 3: Irradiation of PEGA & PFA-treated parylene through glass. Pyrex glass was incorporated into the experimental set-up to filter out wavelengths below 300 nm that might cause oxygen to react with the parylene. The treated parylene surfaces were left open to the air, with only a Pyrex glass barrier between the light source and the surface. The contact angle of the untreated surface did not change, while the hydrophilicity of the PEGA-treated surface increased, but the PFA-treated surface was unchanged (Figure 7).

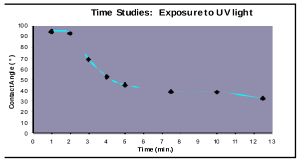


Alternative, 2-step method for hydrophobic surface modification (azido benzoic acid followed by fluorinated amine)

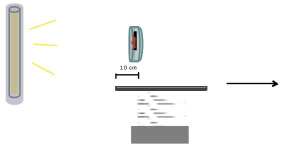
Contact angle before irrad.	Contact angle after acid treatment & irrad.	Contact angle after 2nd step
93˚ ± 2	85 ˚ ± 2	101 ˚ ± 4

Experiment 5: Alternative method for hydrophobic surface modification. Because direct coating with PFA did not increase the hydrophobicity, a two-step method was attempted (scheme shown top, center). The parylene surface was coated with 4-azidobenzoic acid, enclosed in glass and irradiated 10 min, then submerged in a solution of the amine, which has a perfluorinated tail. The contact angle increased from 93 to 101°. (Figure 9).





Experiment 2: UV treatment of parylene in air. UV light was used to modify an uncoated parylene surface to make it more hydrophilic. The parylene surfaces were irradiated for 1-min increments up to 12.5 min at 10 cm distance from the UV lamp. The results show that the parylene surfaces became more hydrophilic as the irradiation time was increased (graph above and Figure 6).



	Uncoated parylene		Coated parylene	
	Contact angle before irrad.	Contact angle after irrrad.	Contact angle before irrad.	Contact angle after irrad.
PEGA	92˚	92˚	89˚	60˚
PFA	92˚	92˚	88˚	88˚

Experiment 4: Irradiation of glass-enclosed PEGA- and PFA-treated surfaces. A Pyrex petri dish was used to enclose the PEGA-and PFA-treated parylene surfaces. The irradiated PEGA-coated surface is more hydrophilic than the original parylene, so the desired surface modification was achieved. The irradiated PFA-coated surface did not become significantly more hydrophobic, so an alternative reaction sequence was tried (Expt. 5). Note that encasing the substrate prevented changes to the untreated parylene. This suggests UV + atmospheric oxygen were responsible for the changes observed in Expt. 1.

Conclusions

Coating parylene surfaces with PEGA and irradiating with UV light changed the water contact angle from ~90 to 60°. Treating parylene with PFA by the same process caused no change in contact angle, but the alternative two-step process (Expt. 5) did make the surface more hydrophobic, increasing the contact angle to ~101˚. These simple wettability modifications were applied to the entire device surface and could be patterned through a mask.

Treating parylene with UV light in air proved to be a fast and simple way to increase surface hydrophilicity. The water contact angle of ~33° was significantly lower than that obtained for the PEGA-treated surface and the method does not require exper-tise in synthesis. A mask can be used to pattern the surface, as shown in Figure 10.

Droplet Images

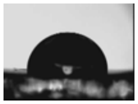


Figure 4. Water droplet on a parylene surface before modification.

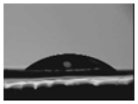


Figure 5. Water droplet on a PEGA-coated parylene surface after 10 min UV irradiation in air. (**Experiment 1**).

Figure 6. Water on parylene after 10 min UV irradiation in air (**Experiment 2**).

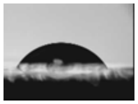


Figure 7. Water on PEGA-coatedparylene surface after 10 min UV irradiation in air w/Pyrex barrier. (**Experiment 3**).

Figure 8. Water on PEGA-coated parylene after 10 minirradiation in a *closed* system (**Experiment 4**).

Figure 9. Water on parylene modified by 2-step fluor-ination (**Experiment 5**).

Figure 10. Pattern created by exposing parylene to UV light through a mask in air. The liquid is dyed water (**Experiment 2**).

Acknowledgments

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