# Annealing Thin-Film Block Copolymers to Achieve Ordered Morphologies

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## Abstract:

A proton exchange membrane fuel cell requires a membrane that selectively allows for the passage of protons. One way to accomplish proton conductivity is to use sulfonated self-assembling block copolymers. The negative charge of the sulfonic acid groups in one of the block copolymer phases imparts the desired cation or proton conductivity. It is likely that the morphology of the film affects the conductivity; however, before the conductivity-morphology connection can be quantified, there must first be an understanding of the morphologies of sulfonated films as well as a reliable way of inducing them. To accomplish morphological control of sulfonated block copolymers, annealing was conducted on unsulfonated and sulfonated systems. The process of annealing uses solvents or heat to allow the polymer to become mobile and the phases to separate and align in reference to each other. This work tests annealing on unsulfonated copolymers, as well as whether sulfonated copolymers can be successfully annealed, and what phases result.

## Introduction:

Block copolymers form morphologies with domains on the order of 10-100 nm due to separation of the different chemical phases of the polymer chain. When the polymers are allowed to move, the different blocks will naturally self-assemble into distinct phases based on the composition and volume fractions of the polymer constituents. By heating a polymer past its glass transition temperature ($T_g$) or using solvent to depress the $T_g$, the polymer chains become mobile and rearrange towards an equilibrium structure.

This work is directed at testing various ways of arranging an unsulfonated block copolymer, and to determine if the behavior of sulfonated copolymer analog is at all similar. Experiments were conducted on poly(hexyl methacrylate)-*b*-polystyrene-*b*-poly(hexyl methacrylate) (PHMA-*b*-PS-*b*-PHMA). This triblock copolymer was chosen due to the low glass transition temperature of poly(hexyl methacrylate). The low $T_g$ allows annealing to be conducted at lower temperatures, decreasing the chances of the copolymer decomposing.

## Methods:

Unsulfonated PHMA-*b*-PS-*b*-PHMA in dioxane and 100% sulfonated PHMA-*b*-PS-*b*-PHMA in dimethylformamide were used. The films were spun cast onto silicon wafers coated with a poly(styrene) brush. After the wafers were rinsed with ethyl alcohol, the brush was made by casting 1% w/v polystyrene in THF, baking under vacuum at 195°C for 2.5 h, and then rinsing away the excess poly(styrene) with toluene. 15 $\mu$L of 0.1 wt % polymer solution were spin cast at 1000, 2000, and 3000 rpm to achieve varying film thicknesses on the order of 100 to 200 nm. The thickness of the spun cast films was measured using profilometry. Samples were subjected to thermal annealing or vapor annealing. Thermal annealing was conducted under vacuum at 180°C for 8 hours with cooling to room temperature under vacuum. Non-selective solvent vapor annealing was conducted under a saturated dioxane atmosphere for the unsulfonated samples and dimethylformamide for the sulfonated samples at 24°C for 24 hours. The samples were examined using atomic force microscopy and field emission scanning electron microscopy.

## Results:

Figure 1 displays the disorganized mixed lamellar and cylindrical morphologies of unsulfonated PHMA-*b*-PS-*b*-PHMA. The morphological domains are 30 to 70 nm in width. Both thermal and vapor annealing increased the order of the unsulfonated PHMA-*b*-PS-*b*-PHMA domains. After annealing, the lamellar structures were aligned parallel to one another with less cylindrical domains.

While the morphologies of Figure 1 are disorganized, Figure 2, a 3000 rpm spin cast sample after vapor annealing, shows aligned morphologies.

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Figure 3 shows an unannealed sulfonated PHMA-*b*-PS-*b*-PHMA spun cast at 1000 rpm. The sulfonated poly(styrene) midblock has aggregated, causing the film to be different than the unsulfonated sample. This morphology does not change with thermal or vapor annealing, which is displayed by Figure 4, a vapor annealed sulfonated PHMA-*b*-PS-*b*-PHMA.

## Conclusions:

The unsulfonated PHMA-*b*-PS-*b*-PHMA triblock copolymer showed disordered morphologies in the as-cast state, but upon either thermal or vapor annealing showed a mixture of aligned lamellar and cylindrical morphology. These results indicate that temperatures of 180°C or the use of a non-selective solvent were sufficient to allow re-arrangement of the phases. Sulfonated PHMA-*b*-PS-*b*-PHMA did not show domain arrangement in the as-cast state and instead showed an aggregated structure that may be a result of the sulfonated polymer's solution behavior. The sulfonated copolymer does not seem to form the same morphologies as the unsulfonated copolymer. Neither thermal nor vapor annealing caused a significant difference in the phase behavior of the sulfonated PHMA-*b*-PS-*b*-PHMA. The aggregated sulfonated PS domains prevented annealing.

## Future Work:

One reason that annealing could not be achieved in the sulfonated sample is that sulfonation has raised the glass transition temperature ($T_g$) of polystyrene such that 180°C is no longer sufficient for annealing. To test this increase in the $T_g$, annealing will be attempted at higher temperatures. Also, as this project only examined 0% and 100% sulfonated copolymer, research will be done on partially sulfonated copolymers to determine if their behavior is intermediate to the unsulfonated or fully sulfonated samples.

## Acknowledgements:

## References:

[1]  Bosworth, J.K., Paik, M.Y., Ruiz, R., Schwartz, E.L., Huang, J.Q., Ko, A.W., Smilgies, D.M., Black, C.T., Ober, C.K. "Control of self-assembly of lithographically patternable block copolymer films." ACS Nano 2. 7 (2008): 1396-1402.

*Figure 1: Unannealed unsulfonated PHMA spin cast.*

*Figure 2: Vapor annealed sulfonated PHMA spin cast.*

*Figure 3: Unannealed sulfonated PHMA spin cast.*

*Figure 4: Vapor annealed sulfonated PHMA spin cast.*