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# Thin Film Block Copolymer Assembly in Mixtures of Highly Selective Solvents

**Christopher J. Ellison,[1] Julia D. Cushen,[1] and C. Grant Willson[1,2]**

*The University of Texas at Austin, Department of Chemical Engineering[1] and Department of Chemistry[2], 200 E. Dean Keeton Stop C0400 Austin, TX 78712*

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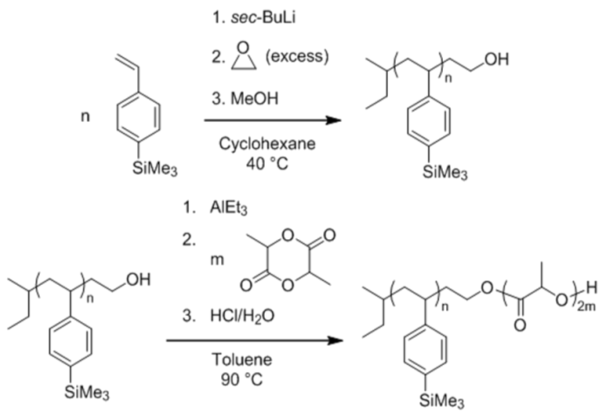
## 1. Introduction

Perpendicular orientation of block copolymer (BCP) domains in thin films is generally preferred over parallel orientation for lithographic applications.[1] Thermal annealing can be used to promote this orientation, but often requires a top coat since one block will typically wet the air interface.[2] Solvent annealing is an attractive alternative for achieving perpendicular orientation of the domains by neutralizing the surface energy of the air interface. Many examples of using solvent annealing in BCP thin films exist in the literature, involving domain non-selective[3] and selective[4] solvents.

Silicon-containing polymers are desirable for lithographic applications because their high chi-parameters and high etch selectivity allow them to self-assemble into small domains and be transferred easily into an underlying substrate by oxygen etching.[5, 6] This paper describes the process used to solvent anneal a new silicon-containing polymer, poly(trimethylsilyl styrene-*b*-lactide) (PTMSS-*b*-PLA) using cyclohexane vapor, a solvent that preferentially swells the PTMSS domain.

## 2. Methods

PTMSS-*b*-PLA was synthesized as previously reported by a combination of anionic and ring-opening polymerization techniques following Scheme 1.[5] Molecular weight and volume fraction were characterized by gel permeation chromatography and nuclear magnetic resonance, respectively. The bulk morphology was characterized by small angle x-ray scattering. As previously reported, a 12.0 kDa lamellae forming sample of this material self-assembles into 15.3nm pitch domains in the bulk after thermally annealing above the glass transition temperatures of both blocks.[5]




Scheme 1. Synthesis of PTMSS-*b*-PLA by anionic and ring-opening polymerization.

Silicon-containing block copolymers are typically difficult to orient by thermal annealing since one block usually preferentially wets the air interface. This is also typical of high chi-parameter materials (PTMSS-*b*-PLA, $\chi$=0.42 at 140°C), since the chemical dissimilarity of the two blocks makes it difficult to neutralize their interfacial energy of the air interface of the thin film.

Because of this, thin films of lamellae-forming PTMSS-*b*-PLA were annealed in a solvent annealing chamber setup described by Figure 1. Nitrogen is bubbled through a solvent reservoir, creating a solvent-rich vapor exiting the reservoir. A nitrogen purge carries solvent vapor to a chamber containing the sample. The vapor swells the film which is monitored *in-situ* by ellipsometry. The solvent swelling gives the BCP enough mobility to reassemble and, upon removal of the solvent vapor, an evaporation front perpendicular to the plane of the substrate can promote perpendicular orientation of the domains.

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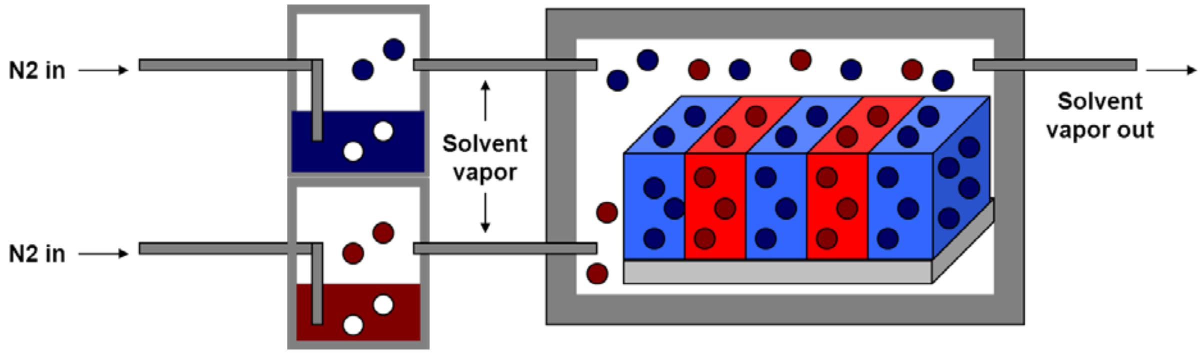

Figure 1. Solvent annealing chamber setup depicting a system with two selective solvents.

While this annealing setup can utilize more than one solvent (two are shown in Figure 1), cyclohexane was first used as a single annealing solvent to facilitate perpendicular orientation of the BCP domains upon annealing. It was concluded that cyclohexane is likely a selective solvent for the PTMSS domain based on the polymer-solvent chi-parameters for the two blocks and cyclohexane. The solubility parameters of cyclohexane, PLA, and PTMSS are 16.8, 20.5, and 17.2 $(MPa)^{1/2}$, respectively, where the solubility parameter of PTMSS is approximated by the group contribution method.[7] The polymer-solvent chi parameter for each domain is estimated by Equation 1, where $V_1$ represents the molar volume of the solvent and $\delta_1$ and $\delta_2$ represent the solubility parameters of the solvent and polymer, respectively.

$$\chi_{P-S} = \frac{V_1}{RT}(\delta_1 - \delta_2)^2 + 0.34 \quad (1)$$

A $\chi_{P\text{-}S}$ less than 0.5 generally means the polymer and solvent are miscible while $\chi_{P\text{-}S}$ greater than 0.5 is characteristic of an immiscible system. Based on these reported solubility parameters, $\chi_{P\text{-}S}$ is 0.347 for PTMSS-cyclohexane and 0.937 for PLA-cyclohexane. Thus, cyclohexane is highly preferential for the PTMSS domain, miscible with PTMSS domains and immiscible with PLA domains.

## 3. Results and Discussion

After solvent annealing the bulk lamellae-forming PTMSS-*b*-PLA, it was discovered by analysis of atomic force microscopy (AFM) images, such as that in Figure 2, that the spacing of the domains increases from 15.3 nm in the bulk to approximately 24 nm in thin films. Previously, it has been shown that highly selective solvents increase the size of block copolymer domains due to an increase in the effective chi-parameter between the blocks when annealing with this type of solvent.[8] An increase in the domain size could also be the result of a change in the effective volume fraction of the blocks when swollen with a selective solvent.[8] Since cyclohexane is preferential for the PTMSS domain, both phenomena likely contribute to the experimental observation of domain size swelling.

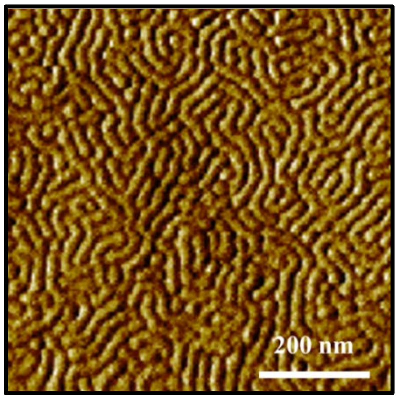

Figure 2. 35 nm thick film of lamellae-forming PTMSS-*b*-PLA after solvent annealing with cyclohexane.

This solvent annealing setup is also being used to investigate solvent annealing with a mixture of selective solvents by adding acetone, a PLA-selective solvent with a solubility parameter of $20.3(MPa)^{1/2}$ [7], to the cyclohexane. With this mixture of highly selective solvents, the effect on thin film self-assembly and domain size is being investigated.

## 4. Conclusions

A new block copolymer, PTMSS-*b*-PLA, was solvent annealed using cyclohexane, a PTMSS-selective solvent based on polymer-solvent chi-parameter values. It was discovered that this setup causes the pitch of the block copolymer to increase due to an increased effective chi parameter between the two blocks and domain swelling effects. Effects of a mixture of selective solvents are being investigated by adding acetone, a PLA-selective solvent, to the annealing setup.

**References**

1. H.-C. Kim, S.-M. Park and W. D. Hinsberg, *Chemical Reviews* ***110***, 146.
2. C. M. Bates, T. Seshimo, M. J. Maher, W. J. Durand, J. D. Cushen, L. M. Dean, G. Blachut, C. J. Ellison and C. G. Willson, *Science***, 338** (2012) , 775.
3. T. P. Lodge, K. J. Hanley, B. Pudil and V. Alahapperuma, *Macromolecules* **, 36** (2003), 816.
4. T. P. Lodge, B. Pudil and K. J. Hanley, *Macromolecules,* **35** (2002), 4707.
5. J. D. Cushen, C. M. Bates, E. L. Rausch, L. M. Dean, S. X. Zhou, C. G. Willson and C. J. Ellison, *Macromolecules,* **45** (2012), 8722.
6. J. D. Cushen; I. Otsuka; C. M. Bates; S. Halila; S. Fort; C. Rochas; J. A. Easley; E. L. Rausch; A. Thio; R. Borsali; C. G. Willson; C. J. Ellison, *ACS Nano***, 6** (2012), 3424.
7. J. Brandrup, E. H. Immergut, E. A. Grulke, A. Abe and D. R. Bloch, John Wiley & Sons.
8. K. J. Hanley, T. P. Lodge and C.-I. Huang, *Macromolecules***, 33** (2000), 5918.