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# Effect of a Glassy-Glassy Polymer Interface on the Physical Aging of Polystyrene

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An abstract of
A thesis submitted to the Faculty of the
James T. Laney School of Graduate Studies of Emory University
in partial fulfillment of the requirements for the degree of
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# Abstract

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Polymers that have been cooled below their glass transition temperature ($T_g$) are amorphous, non-equilibrium solids. Because they are out of equilibrium polymer glasses experience a densification known as physical aging. Here, a thermal reset protocol for use in measuring the physical aging of polystyrene (PS, $T_g$=100°C) in a multilayer polymer film is discussed. Aging rates for single layer bulk films of PS and polycarbonate (PC, $T_g$=145°C) supported on silicon substrates were measured using ellipsometry to test the ability of the protocol to accurately measure physical aging in PS while minimizing aging in PC. Bilayer polymer films were created consisting of PC on PS all supported on silicon. The aging rate of PS in the bilayer system was measured using ellipsometry and found to be consistent with single layer PS values. This newly established protocol may be used for probing the effects on PS of a glassy interface with PC.

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# Chapter 1

# Introduction

Polymers have become an integral part of our daily lives. From natural proteins to synthetic plastics we interact with these macromolecules constantly. Their wide variety and unique physical properties make polymers prime materials for scientific research and commercial industries. As production techniques become more advanced, polymer systems increase in complexity. Gas separation membranes, for example, make use of very thin films[1] and need predictable behavior over time for reliable filtration. Multilayer films often have interesting optical properties for use in data storage[2] or filtering and reflecting light[3]. For these types of applications, it is necessary to understand how the physical properties of a polymer are affected by interfaces with other materials and upon confinement to the nanoscale.

## 1.1 Glass transition

Most polymers will not crystallize and so do not form equilibrium solids when cooled. Instead, they form non-equilibrium glasses[4]. Figure 1.1 shows a schematic of this process. The temperature at which this transition takes place is material dependent and known as the glass transition temperature ($T_g$). Heating a sample above $T_g$ relaxes the polymer to its equilibrium state and can effectively "reset" its thermal history. This process is essential for removing stresses that may have formed in the system during production or storage that could alter the polymer's physical properties. Though clearly not a first-order phase transition (crystallization is a good counter example of a first-order transition), the theoretical mechanisms behind this kinetic transition are not yet well understood. The glass transition is an experimentally observed physical phenomenon where below $T_g$ the molecules simply become frozen in place, thus producing a solid. It is unclear if an equilibrium glass of some sort could be formed through infinitely slow cooling.

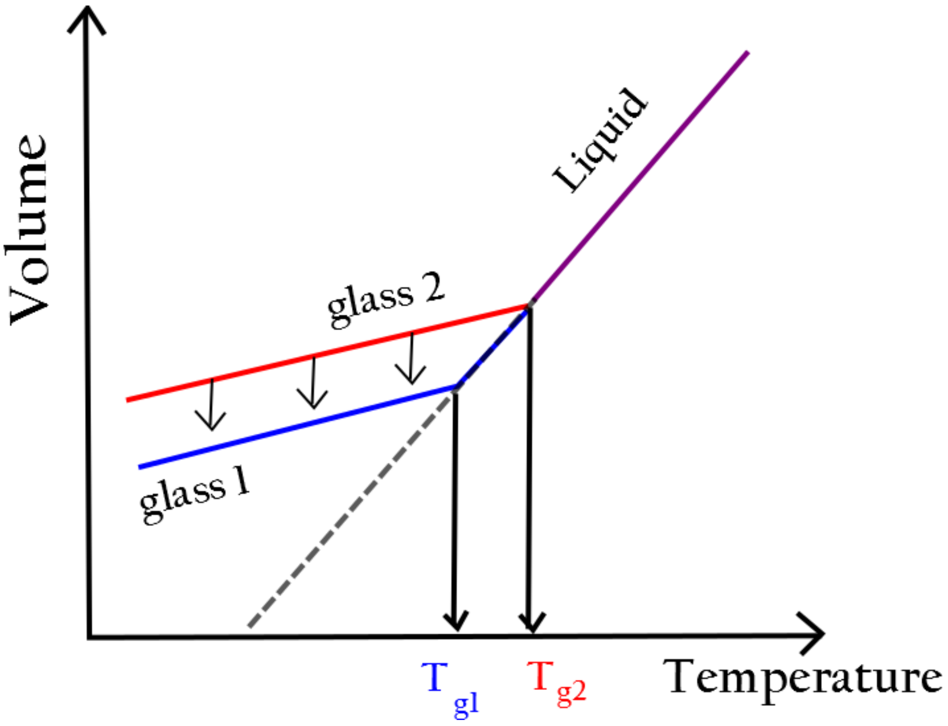


Figure 1.1: This schematic shows the basic behavior of the glass transition. Upon cooling the equilibrium liquid (purple) transitions to an amorphous solid known as a glass (red). Through physical aging the glass approaches equilibrium (dashed) by densifying to a lower energy glass (blue).

## 1.2 Physical aging

Because polymers in the glassy state are out of equilibrium, they experience an energetically driven push to get closer to an equilibrium state. The "empty space" between the polymer chains is referred to as the free volume. Local rearrangements in the polymer segments allow for a decrease in free volume, a release of excess enthalpy, and shift the sample closer to equilibrium. This densification process is known as physical aging[5], and although the volume change is quite small (often only a fraction of a percent), the physical properties (permeability, for example) can be drastically altered[1]. The rate at which the polymer ages is, unsurprisingly, known as the "aging rate" and is often represented by $r$ or $\beta$.

## 1.3 Goal

This thesis describes the method developed for measuring the physical aging rate of polystyrene (PS) beneath a layer of polycarbonate (PC) in order to probe the effects of a glassy/glassy polymer interface in a confined multilayer polymer system. A thermal reset procedure was created to relax the PS ($T_g$ = 100°C) while leaving the PC ($T_g$ = 145°C) undisturbed from its glassy state. Measurements were taken to confirm that the new process minimized effects on the PC while still allowing meaningful results from the PS. Physical aging data were collected on a bi-layer system to demonstrate a proof of concept.

# Chapter 2

# Background

There are many ways to measure the glass transition temperature and physical aging of a polymer film, and the best method may depend on the details of the system being studied. It is important to understand how these methods relate to the core concepts of the glass transition temperature and physical aging in order for results across different methods to be meaningful.

## 2.1 Permeability of gas separation membranes

Permeability is the measure of a material's ability to allow fluids to pass through it. In the case of gas separation membranes that make use of thin polymer films, the amount of free volume in the polymer is related to how easily molecules pass through it. Changes in the membrane's permeability should correspond to changes in the polymer's free volume. A decrease in permeability reflects a loss of free volume and is therefore a sign of physical aging in the polymer. A study by Huang and Paul showed that over the course of 6 months the permeability of $O_2$ through polysulfone had decreased by as much as 50%[1]. The rate at which polymers age is not simply a constant based on the material.

It can be affected by macroscopic changes. Huang and Paul saw a drastic increase in the aging rate for thinner films (less than about 3μm)[1].

## 2.2 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) measures the amount of heat required to increase the temperature of a sample as a function of temperature. Because energy is required to produce a phase change, more heat is needed to steadily increase the sample's temperature during a transition. This causes steps and peaks in the DSC plots, which for polymers, can be used to identify $T_g$ and measure physical aging. The longer a polymer has been in the glassy state, the longer it has been undergoing physical aging, becoming a denser more compact system. It requires more heat to relax an aged glass at the same rate as one that has been newly formed. DSC curves show larger peaks at $T_g$ for glasses that have been aged longer[6]. Example curves are shown in Figure 2.1. Subtracting the reference curve from the aged curve and integrating gives the excess enthalpy (ΔH) recovered upon heating, shown in equation 1.

$$\Delta H = \int_{T_1}^{T_2} \left[C_P^{aged}(T) - C_P^{ref}(T)\right] dT \tag{1}$$

In this case the polymer's aging rate *r* can be calculated from ΔH as seen below in equation 2.[6]

$$r = \frac{d(\Delta H)}{d(ln[t])} \tag{2}$$

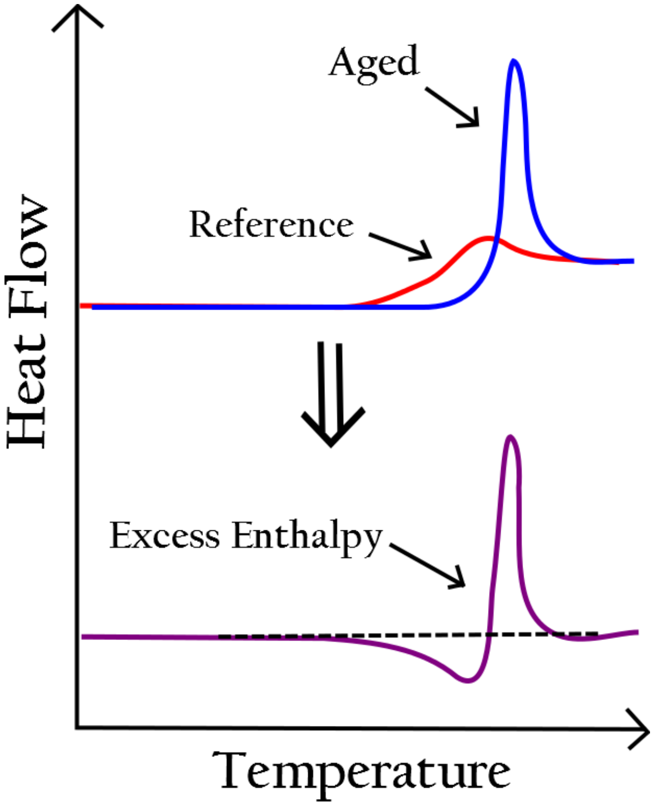


Figure 2.1: Schematic of DSC curves and the process for calculating excess enthalpy. The curve for a polymer aged for 10 minutes, the reference curve (red) is subtracted from that of a polymer aged for 1200 minutes (blue). The resulting curve (purple) can be integrated to attain the recovered enthalpy, used to define an aging rate. Schematic drawn based on data presented in reference 6.

## 2.3 Forced assembly of nanolayers

A relatively new processing method called "forced assembly" takes two immiscible polymers and creates a film made of alternating layers[7]. This is achieved by coextruding two viscosity matched polymers in a single bilayer block, which is then fed through a series of "multiplier dies." These dies cut, stretch, and stack the viscoelastic melt doubling the number of layers and thinning the layer thicknesses with each die. Samples can be produced with thousands of layers only a few nm thick[6].

## 2.4 Glassy-glassy interfaces in polymer systems

Samples of alternating polymer layers of polycarbonate (PC) and poly(methyl methacrylate) (PMMA) formed using the forced assembly process were measured using DSC by Liu et al[7]. When the layers were thick (several hundred nm) the DSC curves revealed two distinct transitions, one corresponding to the $T_g$ of PMMA (112°C) and the other to PC (145°C). However for samples with layer thicknesses below 100nm the transitions begin to merge together shifting toward an intermediate temperature. Below 20nm the transitions are completely indistinguishable and indicate a single $T_g$ between the known glass transition temperatures for PC and PMMA. As the layers become confined to the nanoscale, the interface between the two polymers begins to affect the physical properties of the system as a whole.

A paper by Langhe et al. measures the aging rate of a system of alternating layers of PC (Tg=145°C) and PS ($T_g$=100°C)[6]. DSC measurements show that the aging rate of the PS decreases with decreasing layer thickness. Aging requires a decrease in free volume within the polymer. Having PC present rather than a free surface to confine the PS films may make it more difficult for the free volume to escape, thus decreasing the aging rate of the PS. Chain rearrangements in the PS may be mechanically restricted due to the presence of the PC as well. Another possible explanation for the decrease in aging rate is that though there's no change in the $T_g$ of the pure PS, there is a potential increase in $T_g$ of the interphase material. This could cause longer relaxation times and slower aging rates. As the film thickness decreases, the interphase fraction increases and the aging rate decreases. Because PC has a higher glass transition temperature than PS, it should be possible to thermally reset the PS while leaving the PC in its glassy state (see figure 2.2) as was done by Langhe et al[6]. Owing to the nature of the forced assembly process the PS layer's thickness cannot be controlled independently from the PC layer thickness. At very thin layers it may not be possible to distinguish the DSC peaks for each polymer independently. There is also the constriction of having to measure the behavior of many layers at a time and infer the behavior of a single layer from those results.

It is in trying to eliminate the restrictions listed previously that gives rise to the idea for a simplified experimental setup for a multilayer PC/PS film. I will use a model system of just two layers where each layer thickness can be independently controlled (Fig. 2.3). The focus will be to investigate the feasibility of measuring the physical aging rate of just the PS layer using ellipsometry.

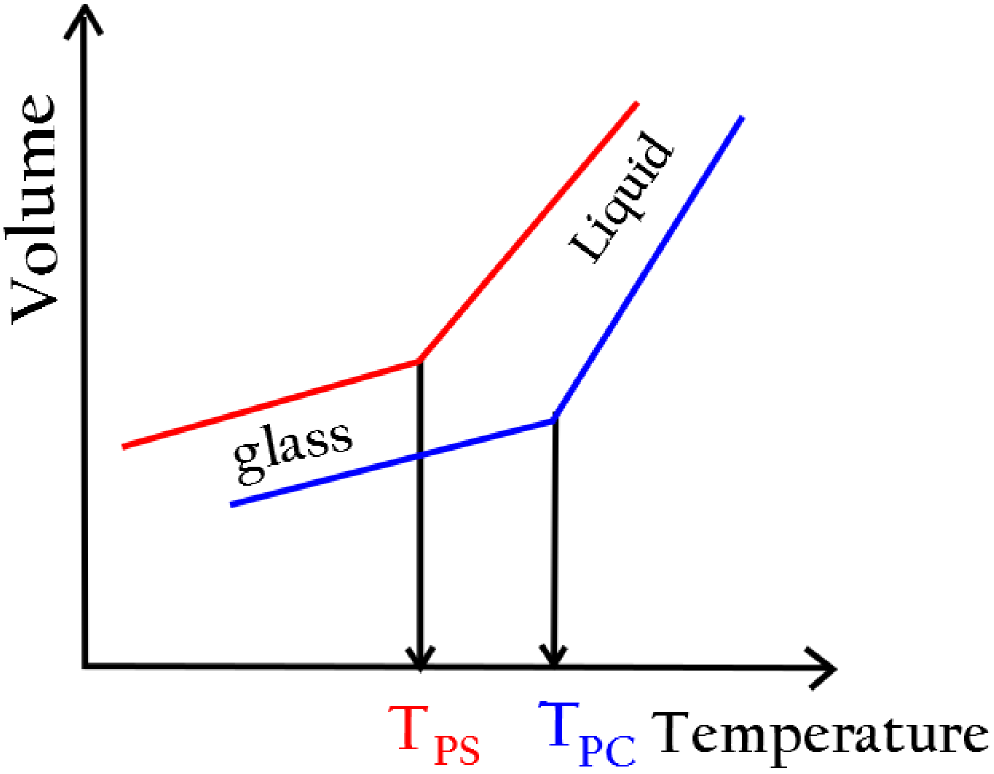


Figure 2.2: Schematic representation of the glass transitions of two polymers, polycarbonate (blue) and polystyrene (red). PC has a higher glass transition temperature than PS. A sample containing PS and PC with both in the glassy state, heated just above the $T_g$ of PS will relax the PS while leaving the PC its glassy state.

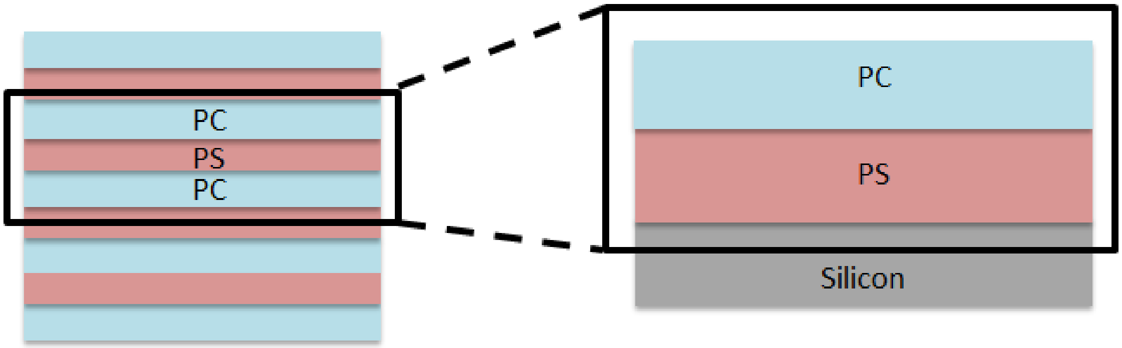


Figure 2.3: Schematic of simplification of the forced assembly multilayer system measured through DSC to a silicon supported bilayer system measured with ellipsometry.

## 2.5 Ellipsometry

Ellipsometry measures the changes in the polarization state of light that has been reflected off of or transmitted through a sample material. This technique is particularly well suited for measuring the physical aging of polymer films as it is sensitive to changes in thickness down to a tenth of an Angstrom. Elliptically polarized light is shone into the sample where it refracts and reflects through the film to be collected by a detector. The electric field $\vec{E}$ of the incident light can be split into components parallel $E_p$ and perpendicular $E_s$ to the plane of incidence. It is the changes in the polarization of the light caused by the interaction with the material that reveal the material's physical properties. The changes in the ellipsometric angles (Δ and Ψ) are used to calculate the total reflection coefficients ($\tilde{R}_\mathrm{p}$ and $\tilde{R}_\mathrm{s}$) using the fundamental equation of ellipsometry:

$$\frac{\tilde{R}_p}{\tilde{R}_s} = \tan(\Psi) e^{i\Delta} \tag{3}$$

A schematic of the reflected and transmitted light from air through a single layer sample on a substrate is shown in Figure 2.4.

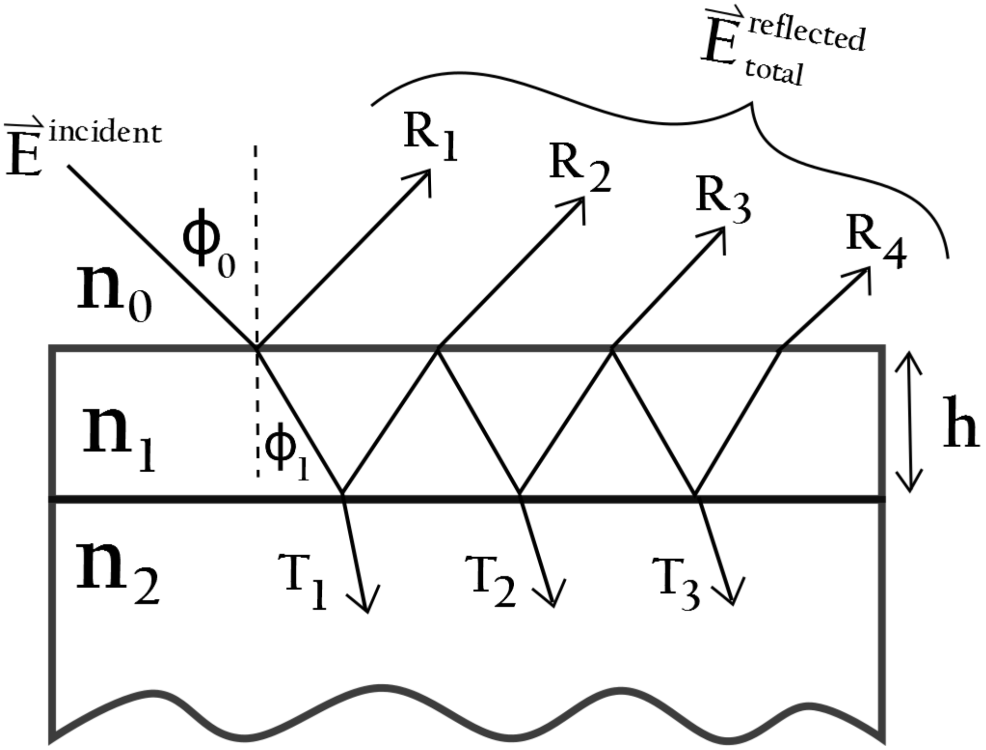


Figure 2.4: Schematic diagram showing light transmitting from air ($n_0$) through a single layer film ($n_1$) of thickness h and a substrate ($n_2$). The substrate can be treated as infinitely thick. Angles of incidence are shown as $\phi_0$ and $\phi_1$. The light reflects and refracts repeatedly throughout the sample.

The Fresnel equations of reflection describe what fraction of light is reflected from an interface between two media. They are related to the index of refraction as follows[8]:

$$r_p = \frac{\tilde{n}_1 cos\phi_0 - n_0 cos\phi_0}{\tilde{n}_1 cos\phi_0 + n_0 cos\phi_0}$$

$$r_s = \frac{\tilde{n}_0 cos\phi_0 - n_1 cos\phi_1}{\tilde{n}_0 cos\phi_0 + n_1 cos\phi_1}$$

(4)

where the complex index of refraction $\tilde{n}$ is the sum of the real part of the index of refraction *n* and the absorption coefficient *k*

$$\tilde{n} = n + ik$$

(5)

The total reflection coefficients relate the total reflected electric field ($E_{total}^{reflected}$) to the incident electric field ($E^{incident}$).

$$\tilde{R}_{p,s} = \frac{E_{total}^{reflected}}{E^{incident}}$$

(6)

The electric field totals can be calculated from the Fresnel coefficients[9]

$$E_{tot}^{ref} = \left(\frac{r_{01} + r_{12}e^{-i2\beta}}{1 + r_{01}r_{12}e^{-i2\beta}}\right)E^{incident}$$

(7)

where the phase difference $\beta = 2\pi\tilde{n}_1 \frac{h}{\lambda} cos\phi_1$ and $\phi$ is the angle of incidence.

To find the index of refraction and thickness of a sample, first a layer model system representing the sample is generated calculating $\Psi^{mod}$ and $\Delta^{mod}$ for varying wavelengths. Then the parameters *h* and *n* are adjusted to minimize the difference between the modeled and the experimentally measured ellipsometric angles. The layer model system typically consists of a silicon wafer substrate (h=1mm – infinitely thick compared to the penetration depth of the incoming light, n~3.8), a native oxide layer (h=2nm, n~1.54), and the polymer film (Fig. 2.5).

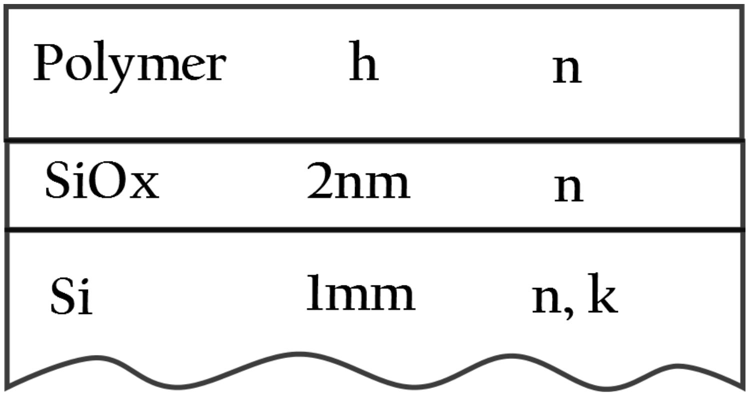


Figure 2.5: Figure shows the model system for a polymer film on a Si substrate. The indexes of refraction for the silicon oxide and substrate layers are taken from the literature. The index of refraction for the polymer layer is estimated through the Cauchy model.

For the polymer film, the index of refraction $n$ as a function of wavelength $\lambda$ for the generated model system is produced using the Cauchy model[9],

$$n(\lambda) \approx A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4} + \cdots \tag{8}$$

where guesses are made for the constants A, B, and C and the thickness $h$. Wavelength dependent values for h and n of SiOx and Si layers are taken as fixed from tabulated values as part of the ellipsometer's software. The fit is adjusted until the modeled and experimental curves of $\Psi$ vs, $\lambda$ and $\Delta$ vs. $\lambda$ match. From these curves $n$ and $h$ values for the polymer film are determined.

A streamlined procedure for using ellipsometry to measure the aging rate of polymer films was developed by Baker et al[10]. PS films were spin coated onto 1 inch squared silicon wafers from a PS toluene solution. They annealed these films under vacuum at 120°C for at least 12 hours. To prep for physical aging measurements they erased the thermal history of the film by placing the samples in a glass Petri dish and annealing again at 120°C for 20-30 minutes. The films were then quenched by placing the Petri dish in contact with an aluminum block at room temperature. The quench rate was ~100°C/min. The polymer samples were placed on a temperature controlled hot stage, and the small changes in the film thickness and index of refraction representing the densification of the film as a function of aging time were monitored resulting in data such as that shown in Fig. 2.4.

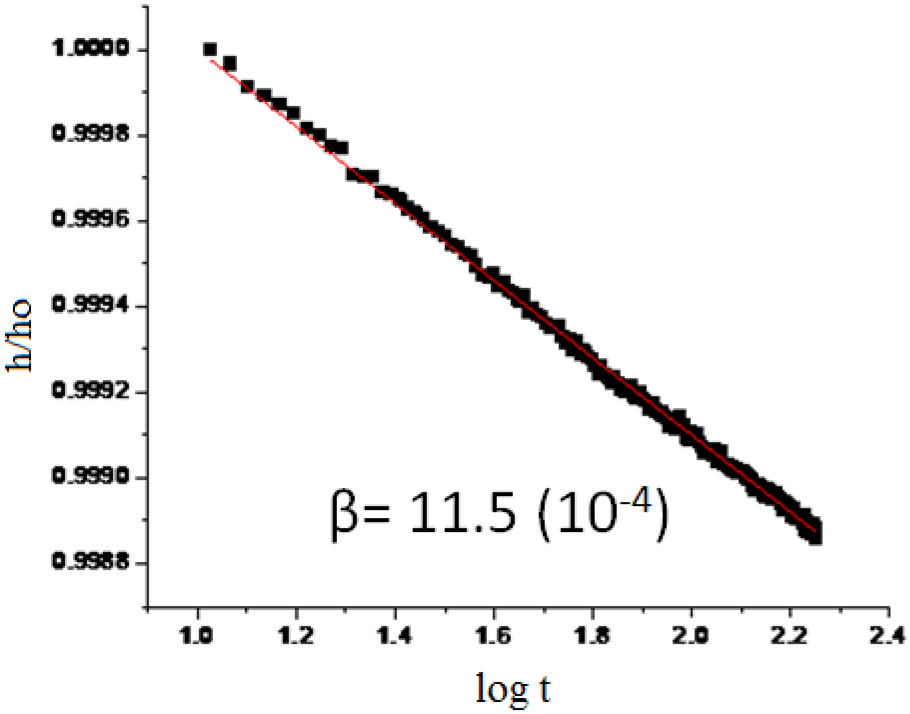


Figure 2.6: Bulk polystyrene film aged for 3 hours, normalized height as a function of log(time) in minutes. Aging rate β as defined from eq. 9.

Measuring every 30 seconds over the course of 6 hours they showed that the aging rate $\beta$ could be determined from the slope of normalized film thickness versus the logarithm of time, shown in Equation 9.

$$\beta = -\left[\frac{\partial h/h_0}{\partial \log(t_a)}\right]_{P,T} \tag{9}$$

## 2.6 $T_g$ and aging of PS

The effect of film thickness on the glass transition temperature of polymers is well studied. The way in which the $T_g$ is affected is polymer dependent. For example, the $T_g$ of PS decreases from the bulk value when film thickness is decreased below ~100nm[11]. The reason for these changes has to do with how interfaces (like that with a free surface or silicon substrate) produce changes in the polymer. Figure 2.5a,b,d shows the effects of free surface and substrate interfaces on PS. Using selective placement of fluorescing dyes, thin layers of PS within a thicker film have their $T_g$ measured[12]. The temperatures shown are the result of the thin layer's $T_g$ minus the accepted $T_g$ value for a bulk film ($\Delta T_g = T_g - T_{g,\ bulk}$). The PS is unsurprisingly unaffected when centered in the bulk, the $T_g$ near the free surface of the film, however, drops by tens of degrees below bulk value. Given the changes seen at the free surface, it makes sense that PS would have a decrease in $T_g$ as the film thickness approaches the length scale of these free surface effects.

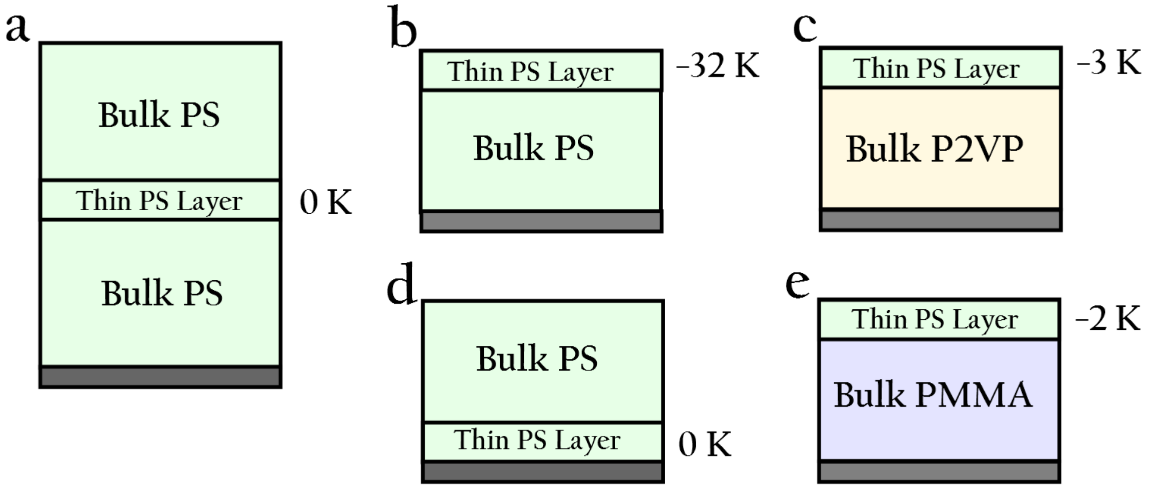


Figure 2.7: Schematic of multilayer polymer systems and the effect on thin PS films. Temperatures shown represent $\Delta T_g = T_g - T_{g,\ bulk}$. Data take from references 11(c and e) and 12(a,b,d).

The aging rate of PS is also affected by decreased film thickness. Pye et al. show that, like the glass transition temperature, the aging rate $\beta$ decreases for thin films below 100nm[13]. At a given aging temperature the aging rate depends on the balancing of two factors. On the one hand the lower the temperature the further the system is from equilibrium and the stronger the drive to rearrange. On the other, there's the fact that molecules will have an easier time rearranging at higher temperatures. Figure 2.6 shows the aging rate as a function of aging temperature for two different PS film thicknesses. Each data point represents the aging rate that is the result of this balancing act, and the peak of the curves shows the optimum temperature for allowing rearrangements in the system. If the decrease in aging rate for thin films was only due to the decrease in average $T_g$, the thinner film's curve would simply be shifted horizontally to lower temperatures while maintaining the same shape and approximate $\beta$ values. To understand this let's assume the change in average $T_g$ is the only thing affecting the aging rate. A decrease in $T_g$ indicates that the optimum temperature for rearrangements has also been decreased and so the peak of the curve will land at a lower temperature, shifting all points in the curve to the left. Clearly this is not the case when comparing the thick and thin films. Pye et al. were able to connect the change in aging rate to the change in local $T_g$ (i.e. reduced at the free surface) in agreement with the data in Fig 2.5a,b,d.

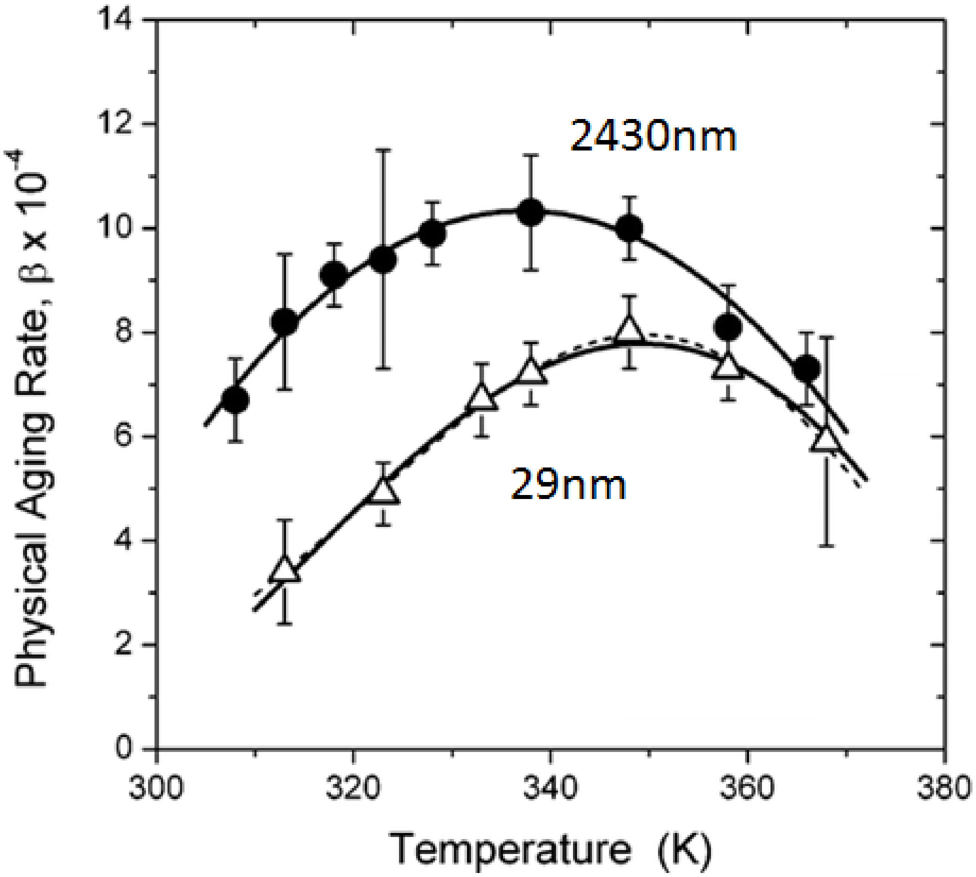


Figure 2.8: Aging rate as a function of aging temperature for a thick (2430nm) PS film and a thin (29nm) PS film[13]. Drop in aging rates and asymmetry of the thin film curve suggests that the changes in aging rate as film thickness decreases are not simply the result of a drop in average $T_g$. [Figure reproduced with permission from Ref. 13]

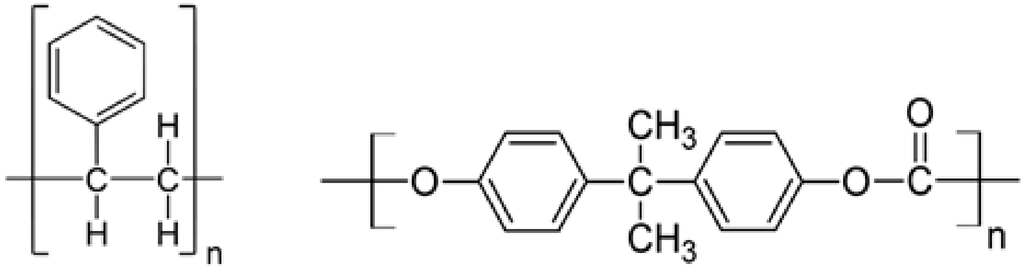
Just as free surface and substrate interactions can affect a polymer's $T_g$ so too can interfaces with other polymers. Work by Roth et al.[11] showed that by creating an interface between a PS film and another polymer, the $T_g$ of the PS can be altered. Figure 2.5 c,e shows that when PS rests on poly(methyl methacrylate) or poly(2vinylpyridine) it’s $T_g$ at the surface only differs from the bulk value by 2 or 3K vs. a 32K decrease from bulk with PS alone. Given that polymer-polymer interfaces affect $T_g$ it is reasonable to investigate how polymer-polymer interfaces may affect physical aging.

# Chapter 3

# Investigating the Physical Aging Behavior of PC/PS Bilayer Films by Ellipsometry

## 3.1 Procedure

This procedure was developed using polystyrene (PS) with $M_w$=280,000g/mol, $M_w/M_n$ =1.5, $T_g$=100°C and polycarbonate (PC) with $M_w$=28,200 g/mol, $M_w/M_n$ =1.7, $T_g$=145°C. The chemical structures can be seen in Figure 3.1.



a) b)

Figure 3.1: Chemical structures of a) PS and b) PC

### 3.1.1 Production of single layer PS and PC films

Film thicknesses of 300-400nm were produced for both polymers. For PS layers the PS was dissolved in toluene at concentrations of 4% wt. Films were formed by spin coating at rates of 1000-3000 rpm onto a 1 inch square silicon wafer. The PS samples were then annealed under vacuum at 120°C for 18 hours to remove residual solvent. For PC layers the PC was dissolved in 1,1,2 trichloroethane at 4-6% wt and spin coated onto a silicon wafer at 3000-5000rpm. The PC samples were annealed under vacuum at 165°C for 18 hours. After annealing, all samples were cooled slowly at less than 1°C/min

### 3.1.2 Production of the bilayer system

The PS layer was produced via the single layer PS method described above; no changes. Production of the PC layer followed the same method, however it was spin coated onto freshly cleaved mica instead of silicon. The layers were annealed separately at their respective $T_g$ + 20°C temperatures. The PC film was cut on the mica into two pieces and floated onto deionized water. From the water one piece of the PC film was caught on a silicon supported PS layer producing a bilayer sample. The other half of the PC film was caught on a clean silicon wafer for independent film thickness measurements. Finally the bilayer was annealed under vacuum at 170°C for 60 minutes to ensure a good polymer-polymer interface, and then cooled slowly at less than 1°C/min. This ensures that the PC layer is well-relaxed on its glassy line.

### 3.1.3 Physical aging

Physical aging measurements were initiated by placing the polymer sample supported by the silicon wafer onto a copper quench plate. A clamp was used to ensure good thermal contact between the sample and the plate. The films were then annealed at 110°C for 10 minutes which for the PS ensures any thermal history is erased, while leaving the PC relatively undisturbed from its glassy state (justification for this departure from the established Baker et al. protocol of 120°C for 20 minutes will be described in detail). To thermally quench the samples they were removed them from the vacuum oven, and the copper plate was put in contact with an aluminum block at room temperature. The Al block and Cu plate remain in contact for 60 seconds with a quench rate of 135°C.[14] The sample is then transferred from the copper plate to the ellipsometer's hot stage stabilized at 65°C. Data of $\Psi$ and $\Delta$ as a function of time are then collected at an angle of incidence of 65° as described in Chapter 2.

## 3.2 Thermal reset protocol

Because the $T_g$ of PS is 45°C lower than that of PC it is possible to reset the aging history of the PS, i.e., reequilibrate the PS layer above its $T_g$ without altering the glassy state of the PC (recall Fig. 2.2). This theoretically should allow the physical aging of the PC to be minimal compared to that of the PS thus isolating the aging characteristics of the PS within a multilayer sample. To develop a reset procedure that would still produce reliable aging in PS while leaving the PC unchanged, I started by measuring the physical aging rate of PS after using the thermal reset protocol outlined by Baker et al[10], and described previously. I also measured the physical aging rate of PC under the same conditions (note this is not an effective reset of PC because 120°C is well below the $T_g$ of PC).

I then decreased the temperature and duration of the annealing procedure to minimize the time spent by PC at a higher temperature. If the polystyrene has been successfully reset it will have the same aging rate for the altered protocol. If on the other hand the reduced heat and duration does not allow the PS to fully relax, its aging rate will appear lower. Figure 3.2 shows that when the change in film thickness of a PC/PS system will be measured by the ellipsometer, it will primarily reflect changes in the PS. It can also be seen that the rate of aging in the PC is negligible under these conditions.

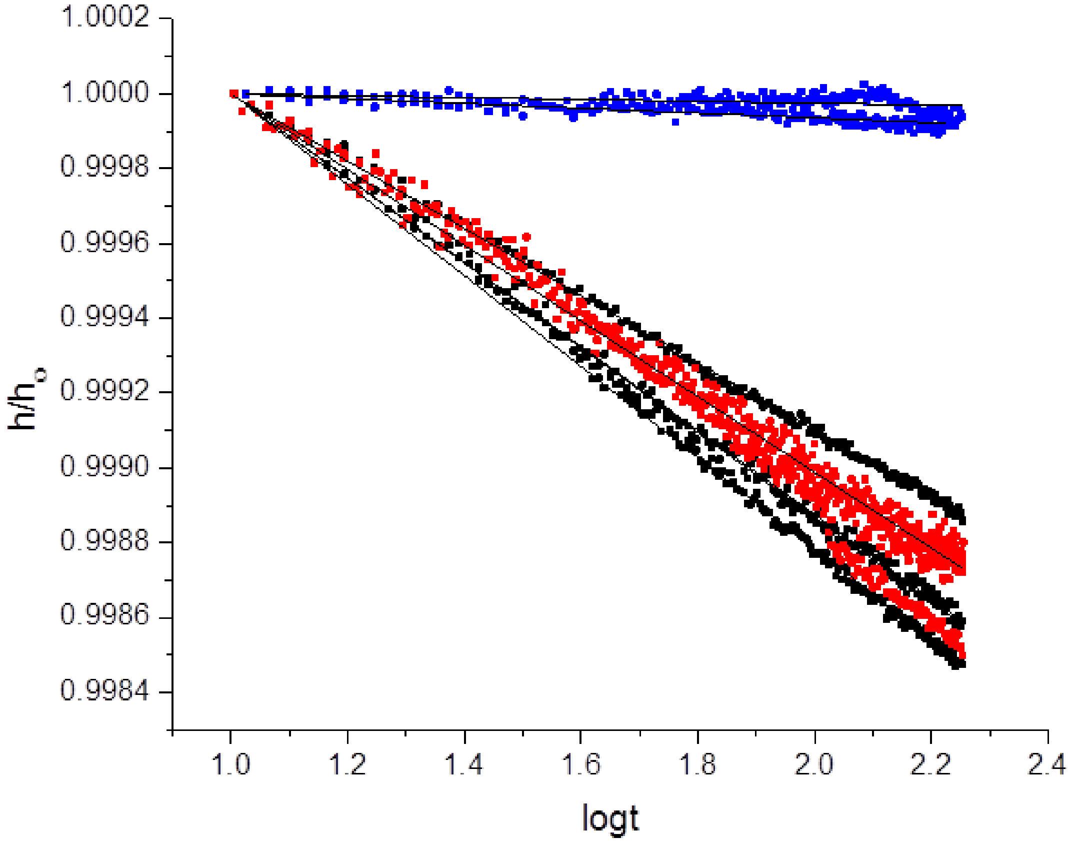


Figure 3.2: Normalized film thickness as a function of log(time) in minutes. Black dots: PS with standard reset protocol, heated at 120°C for 20 minutes (β= [8.5,10, and 12] $*10^{-4}$). Red dots: PS with altered reset protocol heated at 110°C for 10 minutes (β= [9,11, and 11] $*10^{-4}$). Blue dots PC with altered reset protocol, 110° for 10 minutes (β= [0.2 and 0.7] $*10^{-4}$).

The aging rates measured in Fig. 3.2 are determined from equation 5 where the initial film thickness $h_0$ is determined by a 10 minute average of film thickness centered at the 10 minute time mark. It is centered at 10 minutes to be sure the film has reached equilibrium with the ellipsometer's heat stage. The average helps eliminate the effect of noise on the starting point for the best fit line. Figure 3.2 shows that the change in film thickness of a PC/PS system measured by the ellipsometer will primarily reflect changes in the PS. With this new thermal reset protocol the effect of the PC/PS glassy-glassy interface on the aging behavior of PS can be measured.

## 3.3 Bilayer aging measurements

The index of refraction of PC and PS are too similar for the ellipsometer to distinguish the layers as can be seen from the *n* values displayed in Table 3.1. However, because the PC does not age appreciably, changes in the total film thickness can simply be attributed to the PS. The total film thickness as a function of time will be the initial total thickness of the bilayer system minus the thickness lost to aging of the PS layer as shown in Equation 10.

$$h_{total} = h_{0,total} - h_{0,PS}\beta(t_a) \tag{10}$$

This can be used to determine an aging rate of the PS in the bilayer system. The resulting equation for the aging rate is a slightly altered version of Equation 9 and is shown below,

$$\beta = -\frac{1}{h_{0,PS}}\left[\frac{\partial h_{total}}{\partial \log(t_a)}\right] \tag{11}$$

where $h_{0,PS}$ is the initial thickness of the PS layer, and $h_{total}$ is the total thickness of the entire bilayer system, PC+PS. $h_{0,PS}$ is measured on the ellipsometer at room temperature after undergoing the previously described annealing procedures and before the addition of the PC layer. This method for determining $\beta$ has been shown to be valid for a PS/PnBMA bilayer, where the PS and poly(n-butyl methacrylate) (PnBMA) layers can be resolved independently due to differing indices of refraction[15].

Figure 3.3 shows aging runs for two bilayer PC/PS systems. The aging rates for the PS layers are consistent with the aging rates of single layer PS. These results demonstrate that it should be feasible to measure the aging rate of the PS layer within the PS/PC bilayer.

Table 3.1 Measured indexes of refraction (for $\lambda$=632.8nm) from elliptically polarized light for samples of single layer PS and PC and the PC/PS bilayer samples.

| Sample | Index of refraction (n) |
|---|---|
| PS | 1.5721 ± 0.001 |
| PC | 1.5718 ± 0.001 |
| PC/PS | 1.5727 ± 0.002 |

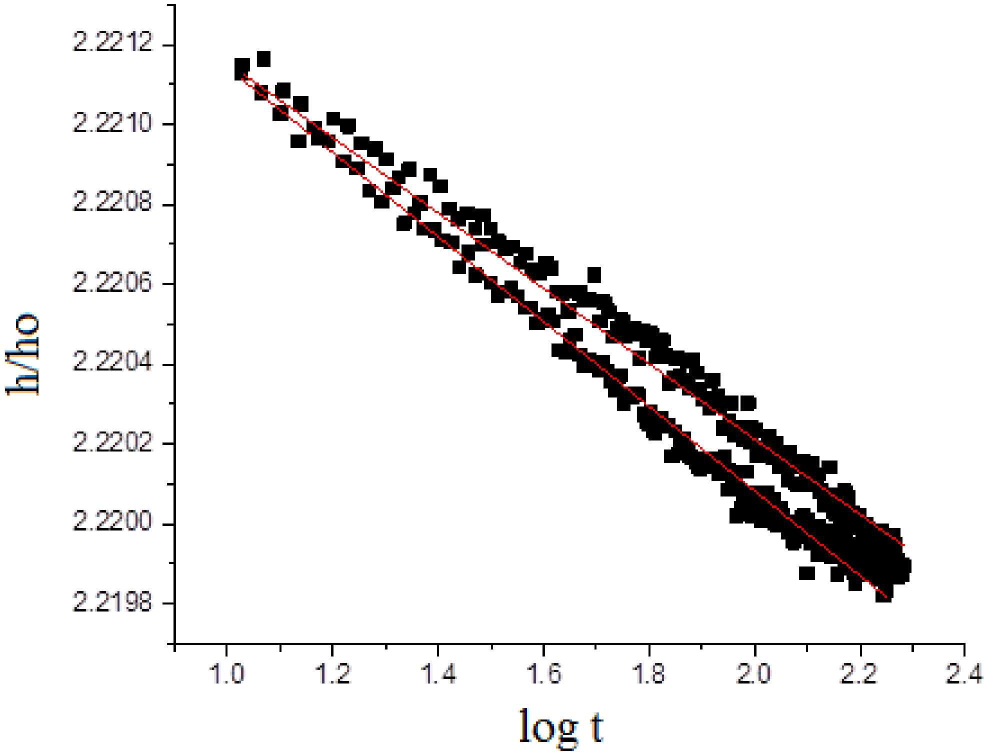


Figure 3.3: Normalized thickness vs log (time) in minutes of two bilayer PC/PS films. Upper data set $\beta$=9.4*$10^{-4}$ ($h_{0,PS}$=329nm, $h_{0,PC}$=372nm), lower data set$\beta$=10.6*$10^{-4}$ ($h_{0,PS}$=305nm, $h_{0,PC}$=372nm).

# Chapter 4

# Conclusions and Future Work

I developed an experimental protocol that can thermally reset PS without resetting PC from its glassy state. Aging rate measurements of individual single layers using ellipsometry confirm the protocol's success. I measured the aging rate of the PS layer within a PC/PS bilayer film. This demonstrated a "proof of concept" experimental protocol that can be used to probe the effects of a glassy-glassy polymer interface on the aging rate of PS.

To further examine the effects of the glassy PC on glassy PS, the reverse bilayer (PS on PC), as well as a trilayer system (PC/PS/PC) could be created. Perhaps most useful in probing the interfacial effects would be decreasing the PS thickness away from the bulk and into the thin film regime. As the aging of single layer thin PS films is well documented, changes in its aging rate when in contact with PC may reveal the length scale of the interfacial interactions between the two polymers. PC is far from the only polymer with a higher $T_g$ than PS (polysulfone is also a good candidate) and so there are a wide range of glassy polymers that could take its place to find the differences between glass/glassy interfaces.

Physical aging and how it is affected by polymer interfaces is still poorly understood. My experimental protocols open a door for experiments involving glassy/glassy polymer interfaces, which may probe the changes seen in the physical aging behaviors of multilayer polymer films.

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