Effect of Adjacent Hydrophilic Polymer Thin Films on Physical Aging and Residual Stress in Thin Films of Poly(butylnorbornene-*ran*-hydroxyhexafluoroisopropyl norbornene)

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ABSTRACT

The properties of thin supported polymer films can be dramatically impacted by the substrate upon which it resides. A simple way to alter the properties of the substrate (chemistry, rigidity, dynamics) is by coating it with an immiscible polymer. Here we describe how ultrathin (ca. 2 nm) hydrophilic polymer layers of poly(acrylic acid), PAA, and poly(styrenesulfonate), PSS, impact the aging behavior and the residual stress in thin films of poly(butylnorbornene-*ran*-hydroxyhexafluoroisopropyl norbornene), BuNB-*r*-HFANB. The aging rate decreases as the film thickness (*h*) is decreased, but the extent of this change depends on the adjacent layer. Even for the thickest films (*h*>500 nm), there is a decrease in the aging rate at 100 °C when BuNB-r-HFANB is in contact with PSS. In an effort to understand the origins of these differences in the aging behavior, the elastic modulus and residual stress (σ_R) in the films were determined by wrinkling as a function of aging time. The change in the elastic modulus during aging does not appear to be directly correlated with the densification or expansion of the films, but the aging rates appear to roughly scale as $h\sigma_R^{1/3}$. These results illustrate that the physical aging of thin polymer films can be altered by adjacent polymers.

INTRODUCTION

The effect of confinement of glassy polymers to nanoscale dimensions can dramatically influence their properties.¹⁻³ The large decrease in the glass transition temperature (T_g) of polystyrene (PS) on nanoconfinement reported by Keddie and Jones⁴ in 1994 has inspired decades of work in examining the dynamics of thin films of PS.⁵ Sensitivities to the nature of the film (e.g., supported vs. free standing),⁶ details of the substrate interactions,⁷ and the averaging dependencies of the measurement techniques^{8,9} have led to some disagreements about the nature of size dependent properties of glassy polymers.¹⁰ The properties of PS examined under nanoconfinement have expanded over the years to include creep compliance,¹¹ viscosity,¹² elastic modulus,^{13,14} and physical aging^{15,16} amongst others. A variety of these measurements have found that the length scale associated with the changes in some of these properties can be substantially greater than observed for T_g.^{17,18}

For membrane applications, these thickness dependent properties can lead to challenges as thin membranes are desired to maximize the flux.¹⁹ Seminal work from Paul and coworkers has demonstrated that physical aging rates can



be dramatically increased for thinner membranes,²⁰⁻²² which leads to a rapid loss of flux due to densification. As these highly selective polymer membranes are commonly supported on macroporous polymers, understanding how the support influences the aging rate of a membrane is highly relevant to these technologies.

Roth and coworkers have demonstrated that both T_g and the physical aging rate of polymer thin films can be dramatically altered by adjacent polymer layers.²³⁻²⁵ In the case of PS on a rubbery polymer, poly(n-butyl methacrylate), the aging rate does not appear to be coupled to the changes in Tg,²⁵ unlike aging for PS supported directly on a silicon water.²⁶ Evans et al. have reported on the influence of the modulus, T_{g} , and fragility of adjacent layers on the changes in glass transition of ultrathin PS films.^{27,28} Similarly, Priestley and coworkers showed that aging in polymer nanoparticles is significantly varied if the nature of the confinement is hard or soft.²⁹ Polymers infiltrated into packed inorganic nanoparticles exhibit significant differences in behavior compared to the supported film,^{30,31} which further illustrates the importance of the local environment on the physical properties of confined polymers.^{32,33} These results have implications in a variety of applications where thin films of polymers are utilized, especially for membrane separations.³⁴

One emergent membrane application is the pervaporation of butanol in the development of next generation biofuels.³⁵ High T_g polymers should decrease the propensity for physical aging at the operating conditions for such membranes,^{36,37} so polynorbornene membranes with high selectivity for butanol and having T_gs in excess of 300 °C are promising candidates for bio-butanol production.³⁸ Recently, we had reported the unexpected rapid aging of similar polymers at temperature >200 °C below T_g when supported on silicon wafers.³⁹ For the thinnest films, the films expanded during isothermal aging.³⁹ A similar isothermal expansion in thin films was reported for polycarbonates,⁴⁰ which

similar to the polynorbornenes contain rigid cyclic rings in the polymer backbone. For the polycarbonates, this effect was attributed to chain distortion by the film boundaries and the expansion was reversible on heating/cooling through T_g .^{40,41} The thermal expansion behavior of the polycarbonate could be modulated with passivated silicon as the substrate⁴⁰ to suppress expansion, which suggests that the interaction of the polymer with the substrate is important in the expansion behavior in thin films.

Here, we examine how ultrathin (ca. 2 nm) poly(acrylic acid), PAA. and poly(styrenesulfonate), PSS, layers on the substrate impact the aging behavior of poly(butyInorbornene-ran-hydroxyhexafluoroisopropyl norbornene), BuNB-r-HFANB, thin films. These two polymers were selected to facilitate removal of the BuNB-r-HFANB films for additional characterization. To understand the differences in the aging behavior as a function of both film thickness, h, and the substrate chemistry, the residual stress, σ_{R} , in the film was determined at different aging times using surface wrinkling⁴², as Roth and coworker had reported that physical aging in thin films can be explained in terms of the stress state of the film.43,44 The determined aging rates for the BuNB-*r*-HFANB films were found to approximately scale with the initial film properties as $h\sigma_{\rm R}^{1/3}$. These results suggest that the stress state that develops during casting of high T_g polymer membranes can impact the aging behavior.

EXPERIMENTAL SECTION

Materials.

Equipment and instruments or materials are identified in the paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology (NIST), nor does it imply the materials are necessarily the best available for the purpose. Toluene (\geq 99.5%, ACS reagent), tetrahydrofuran (THF, \geq 99.5%, ACS reagent) and polyacrylic acid (PAA, nominal M_w = 70,000 g/mol, where M_w is the mass average molecular mass) were obtained from Sigma-Aldrich and used as received. Polystyrene sulfonate (PSS, nominal M_w = 100,000 g/mol) was obtained from PolySciences, Inc. Milli-Q water (18.2 MΩ resistance) was used as the solvent for casting the PAA and PSS.

A random copolymer of butyl norbornene (BuNB) hydroxyhexafluoroisopropyl and norbornene (HFANB), (BuNB-r-HFANB, M_n = 120.2 kg/mol, where M_n is the number average molecular mass), was obtained from Promerus, LLC (Brecksville, OH). The BuNB-r-HFANB was synthesized catalyzed by addition polymerization. The composition was 50 mol% BuNB as determined from ¹³C nuclear magnetic resonance spectroscopy. The glass transition of temperatures (T_g) the associated homopolymers are approximately 340 °C for BuNB and 360 °C for HFANB.45

Polydimethylsiloxane (PDMS, Dow Corning Sylgard 184) was prepared at 20:1 base:curing agent ratio. The PDMS mixture was hand mixed for 10 min and was then poured onto glass to generate a sheet that was \approx 2 mm thick. The PDMS was allowed to rest at room temperature until no bubbles were observed (at least 1 h). The PDMS sheet was then cured at 115 °C for 3 h. The elastic modulus of the PDMS was determined from tensile measurements at a strain rate of 0.01 cm/s using an Instron material testing machine (Instron Model 5567). The PDMS specimen was 25 mm × 75 mm × 2 mm with a gauge length of 50 mm.

Film Preparation.

Silicon wafers (University Wafer, 1-30 Ω ·cm, 500 μ m thick) that were cleaved into approximately 2 cm × 2 cm pieces and cleaned by ultravioletozone (UVO, Jelight Company, Model No. 42) for 30 min were used as substrates. Dust particles were removed using a nitrogen stream with a cleanroom N₂ gun (TA-NITRO-2).

The BuNB-r-HFANB copolymer was dissolved in toluene:THF mixture (1:1 by mass) and stirred for at least 20 min prior to film casting. Films were prepared by spin coating (Laurel Technologies, Model WS-400B-6NPP/LITE) onto cleaned silicon substrate at 262 rad/s (2500 rpm) for 50 s. The thickness of the BuNB-r-HFANB films was controlled by the solution concentration. In some cases, the cleaned silicon substrates were modified by a thin hydrophilic polymer (either PAA or PSS) film prior to coating with BuNB-r-HFANB. Films approximately 2 nm thick were prepared by spin coating at 2500 rpm for 50 s from 0.8 % by mass PAA or 0.5 % by mass PSS in water. These thin films were then dried under vacuum at room temperature for 30 min to remove residual water. The BuNB-r-HFANB film was then spun coat on top of the hydrophilic polymer under the same conditions as used previously. The toluene:THF mixture does not alter the thickness of the PAA or PSS layers, even when soaking the film in excess solvent overnight (Figure S14). The aging of these films was measured within 12 h of spin coating in all cases.

Characterization.

The film thickness was determined via spectroscopic (UV/Vis/NIR) ellipsometry (J.A. Woollam Co., M-2000UI). Significant thermal degradation³⁹ of the BuNB-*r*-HFANB films (Figure S9) occurred prior to reaching T_g (~200 °C), which prevents the thermal history of the films from being erased by annealing above T_g prior to aging studies as is common.¹⁵ Instead, the aging procedure involved heating the spun-coat sample at 100 °C on a preheated sample stage (J.A. Woollam Co., HTC-100). The sample was quickly aligned (<10 min) and ellipsometric angles, ψ and Δ , were measured over the wavelength range λ (243 nm to 1680 nm), at a fixed incidence angle of 70° every 10 min with a data acquisition time of approximately 20 s per measurement. These measurements continued for approximately 17 h.



The film thickness, h, and refractive index, n, were determined using recursive fits of ψ and Δ using a Cauchy model for the optical properties of the BuNB-*r*-HFANB film. In an attempt to avoid heating artifacts,^{36,46} the initial film thickness, h_o , was taken to be the film thickness after the sample was held at 100 °C for 10 min. This time was sufficient to reach the intermediate aging regime for the thickest films examined. This protocol is analogous to prior thin film aging studies^{15,47} with the exception of not annealing the film above T_g prior to aging due to degradation. Following the work of Roth and coworkers,¹⁵ the aging rate (β) was calculated as:

$$\beta = -1/h_o \, dh/d(\log t) \tag{1}$$

where *h* is the thickness of the film at time *t*, *t* = $t_T - t_0$, t_0 is the offset time for heating where h_0 is determined, and t_T is the total time that the film has been held at the aging temperature of interest. After the aging studies were completed, the film was immediately quenched on a metal block at ambient temperature.

For determining the residual stress in the films, the aged polymer film was then transferred to a pre-stretched (~15 % strain) PDMS sheet (25 mm × 75 mm × 2 mm).⁴⁸ A direct transfer method was used through first allowing the PDMS to wet the surface of the film and then using water assisted delamination to remove the polymer film from the substrate while the film remains adhered to the PDMS. After transferring the film, the sample was dried overnight under ambient conditions before the films were wrinkled by reducing the pre-stretch of the PDMS. At ambient temperature, there is no statistical change in the thickness of BuNB-r-HFANB films over 1 week (Figure S15), so this drying process should not influence the aging of the films. The strain was controlled with a linear actuator (Newport, 850G actuator) and a motion controller (Newport, Universal Motion Controller/driver, ESP100). The strain was slowly released at 0.01 cm/s in steps of 0.02 % strain. At each strain step, the surface of the film was imaged using a 3D optical profilometer (Zeta 3D Optical Profilometer, Zeta Optics Module) attached to a camera (Grasshopper 2 Digital Camera, GS2-FW-14S5C). These 3D images enable determination of the wavelength, λ , and amplitude, A, of wrinkles at each strain and aging condition. From λ , the elastic modulus of the BuNB-r-HFANB film, $E_{\rm f}$, was determined using equation 2, following the work of Stafford and coworkers.⁴⁹

$$\lambda = 2\pi h \left(\frac{\overline{E_f}}{3\overline{E_s}}\right)^{\frac{1}{3}}$$
(2)

where *h* is the film thickness, and E_s is the substrate (PDMS) modulus. The critical strain for the wrinkling instability, ε_c , can be calculated using equation 3:

$$\varepsilon_c = \frac{1}{4} \left(\frac{3\overline{E_s}}{\overline{E_f}} \right)^2$$
(3)

Any applied strain above the critical strain serves to increase the amplitude of the wrinkling pattern. Any residual stress/strain in the system acts to alter the observed amplitude of the wrinkles, as given by equation 4:

$$A = h_{\sqrt{\frac{\varepsilon_A}{\varepsilon_c + \varepsilon_R}} - 1} \tag{4}$$

where A is the wrinkle amplitude measured from 3D images, h is the film thickness, and ε_A is the strain applied to the film. This residual stress/strain is initially caused by vitrification during the film coating process but will evolve as the structural relaxations occur due to the pinning by the substrate. The residual strain can be readily translated to the residual stress through the elastic modulus as shown in equation 5:

$$\sigma_R = \varepsilon_R \overline{E_f} \tag{5}$$

The residual stress determined from this method has been demonstrated to quantitatively agree with standard wafer curvature measurements.⁴² In all cases, the error bars presented herein represent one standard deviation of the data,

which is taken as the experimental uncertainty of the measurement.

RESULTS AND DISCUSSION

The local environment for the polymer film is known to play an important role in the observed effect of nanoconfinement.^{50,51} Figure 1A illustrates the geometry of the samples examined here. The BuNB-r-HFANB film was directly formed on a silicon wafer or deposited onto a polyelectrolyte layer, either 2 nm PAA or a 2 nm PSS layer, on a silicon wafer. These three different local environments were selected to understand the effect that the substrate has on the physical aging and mechanical properties of thin BuNB-r-HFANB films. The hexafluoroisopropanol group can hydrogen bond with the surface silanols (silicon wafer), carboxylic acid (PAA) and sulfonic acid (PSS) groups. Prior spectroscopic studies have demonstrated that the relative strength of the hydrogen bonding of hexafluoroisopropanol depends on the chemistry of the associating group.⁵²⁻⁵⁴ From these model studies, it would be expected that the HFANB would associate in terms of strength as PSS > PAA > silanol. Strong favorable interactions between polymer and substrate, such as hydrogen bonding, can significantly influence the observed glass transition temperature⁵⁵⁻⁵⁷ and polymer dynamics⁵⁸ in ultrathin films. Additionally, favorable interactions of the polymer with the substrate can slow physical aging near the substrate relative to the bulk.59-61

Figure 1B shows the normalized film thickness as a function of aging time for $\approx 1 \ \mu m$ thick BuNB-*r*-HFANB films that are supported on clean silicon wafer (black), 2 nm PAA film (blue), and 2 nm PSS film (red). All films were aged at 100 °C for ≈ 17 h. For these thick films, the aging of the BuNB-*r*-HFANB films is independent of the underlying support. This similarity in aging of the thick films suggests that the physics of film formation is not radically altered by the underlying support.



FIGURE 1. (A) Schematic of film geometry examined. Physical aging of BuNB-*r*-HFANB at 100 °C on clean silicon (black), 2 nm PAA (blue), 2 nm PSS (red) for (B) \approx 1 µm thick and (C) \approx 150 nm thick films.

However, when the film thickness is decreased from $\approx 1 \ \mu m$ to $\approx 150 \ nm$, the substrate significantly impacts the aging behavior of the BuNB-*r*-HFANB film when aged at 100 °C. As shown in Figure 1C, the film thickness of the BuNB-*r*-HFANB initially decreases during aging as expected for all substrates, but after approximately an hour of aging at 100 °C the rate of aging decreases for all films. The aging rate (i.e., the observed decrease in film thickness) is clearly dependent on the underlying support for the BuNB-*r*-HFANB film. On PSS, the the BuNB-*r*-



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HFANB film (145 nm thick) exhibits the slowest decrease in film thickness during aging. In this case, the film thickness surprisingly starts to increase after around 80 min. This increasing film thickness during aging has been reported previously for thin spin cast films that were not annealed above T_g prior to aging.^{39,62} This increase is attributed to the highly non-equilibrium chain conformations induced during rapid vitrification associated with spin coating. Interestingly after 1000 min of aging, the thickness of the BuNB-r-HFANB film on PSS was almost unchanged from its initial thickness (h/h_o = 1.001).

On a clean silicon wafer, the initial aging rate is greater than for the film on PSS. At around 80 min of aging, the film thickness becomes nearly invariant until approximate 600 min of aging, after which time the film thickness begins to increase with the final thickness being similar to the initial thickness ($h/h_{\circ} = 0.999$). For the substrates examined, the ≈150 nm thick BuNB-r-HFANB films age most rapidly initially when supported on 2 nm PAA. Similar to the film on the clean silicon wafer, the film thickness becomes invariant after approximately 80 min of aging. After ≈400 min, the film thickness slowly increases. These results illustrate that the substrate impacts the aging behavior in films of BuNB-r-HFANB that are approximately 150 nm thick. Although this is greater than the length scales commonly observed for changes in T_g from nanoconfinement,^{2,63,64} the aging of thin films can be influenced by nanoconfinement over 100's of nm.¹⁷

Figure 2 illustrates the impact of film thickness on the physical aging of the BuNB-*r*-HFANB films at 100 °C on the three different supports. For all three substrates, the aging rate tends to decrease as the thickness of the BuNB-*r*-HFANB film decreases below some threshold thickness. On clean silicon wafers (Figure 2A), the aging behavior is effectively independent of thickness for films thicker than 700 nm. For films thicker than 150 nm, the film thickness initially decreases similar to the thicker films, but the

rate of densification decreases at longer times. As the initial film thickness is reduced, this deviation from the intermediate aging behavior occurs sooner in the aging process. The slowdown in the aging occurs after ≈300 min for the 500 nm film and \approx 80 min for 150 nm. For thinner films, non-monotonic changes in film thickness are observed, where the film thickness initially decreases, but within the first hour of aging the film thickness begins to increase. The final thickness after 17 h of aging can exceed the original thickness with $h/h_0 = 1.0015$ for 80 nm and h/h_o = 1.0006 for 50 nm films of BuNB-r-HFANB on clean silicon wafers. This nonmonotonic aging behavior is reproducible (Figure S1).



FIGURE 2. Thickness dependent physical aging of BuNB-*r*-HFANB at 100 °C on (A) silicon, (B) 2 nm PAA film, (C) 2 nm PSS film. The aging was measured continuously over 17 h. Decreasing thickness tends to lead to reduced initial aging rate, but also for the thickness to increase at long times. Approximate film thicknesses: 50nm, 80nm, 115nm, 150nm, 250nm, 400nm, 500nm, 600nm, 700nm, 960nm, and 1200nm.

The appearance of the thickness evolution during aging when the substrate is coated with a 2 nm thick layer of PAA is similar to the previous case of the clean silicon wafer as shown in Figure 2B. The aging rate again generally decreases with decreasing film thickness, but the aging slows considerably at long times even for a 960 nm films. The non-monotonic aging is observed for films as thick as 115 nm, but the film was densified after 1000 min of aging at 100 °C. For 90 nm thick film, the initial decrease in thickness is small and after 400 min of aging, the thickness begins to increase rapidly. This results in a thicker film (h/h_{\circ} = 1.002) after 1000 min of aging. For the 50 nm thick film, the thickness does not initially decrease like in the other cases but remains relatively constant (oscillates slightly) until approximately 200 min when the thickness begins to increase, again leading to a thicker film after 1000 min of aging.

Examination of Figure 2 can lead to the conclusion that the inclusion of a 2 nm layer of PSS dramatically impacts the aging behavior of the BuNB-*r*-HFANB films (Figure 2C). None of the films examined exhibit constant aging rates that would be expected within the intermediate aging regime. The non-monotonic aging behavior for the BuNB-r-HFANB films on PSS is observed for films as thick as 250 nm. The film thickness begins to increase after approximately 100 min of aging for films from 250 nm to 90 nm More interestingly, the thickness thick. continuously increases for a 45 nm film during aging. Figure S17 more clearly illustrates the full extent of the expansion over 1000 min. We attribute this behavior to the non-equilibrium chain conformation induced by the spin coating, associated with the pancake-like morphology of spin cast ultrathin polymer films,65 where relaxation towards equilibrium may require the films to expand. The isothermal expansion of ultrathin films has been reported for polycarbonates (PC) when the film thickness is similar to Rg.^{40,41} This expansion of PC films is reversible on heating/cooling through T_g to demonstrate that this expansion is not from dewetting. Unfortunately, the thermal stability of the BuNB-*r*-HFANB prohibits heating above T_g without chemical degradation, but there is no evidence for dewetting or void formation from AFM after aging (Figure S13). Both PC and BuNBr-HFANB contain rigid cyclic groups in their backbone with two aromatic rings from the bisphenol A in PC and the bicyclic ring of the norbornene on every monomer in BuNB-r-HFANB. The cyclic groups in the backbone is a distinguishing feature for these polymers in comparison to most other polymers commonly examined for thin film studies and the isothermal expansion below T_g may be a common phenomenon in polymers with this structure, but additional studies of other polymers with cyclic groups in their backbone are required.

To more quantitatively examine the effect of the thin PSS and PAA layers on the aging of the BuNB-r-HFANB films, the initial aging rates (β) were determined from the initial linear region (h/h₀ vs log time) where present as shown in Figure 2. Representative fits to determine these aging rates are shown in Figure S2. Figure 3 illustrates the thickness dependence of the calculated aging rates of BuNB-r-HFANB films on the three different substrates. For the thickest films (>1 μ m) examined, the aging rates for the BuNB-r-HFANB films are modestly accelerated on the thin (ca. 2 nm) polymer layers in comparison to the clean silicon wafer. This length scale is consistent with the gradients in aging rates determined from fluorescence measurements.¹⁷ Bagley and Roth have shown that T_g gradients across polymer-polymer interfaces can extend 100's of nm when there is a large mismatch in T_g between the polymers.²⁴ Here, there is a large difference in T_g between



the BuNB-r-HFANB (\approx 350 °C) and PAA (\approx 106 °C) or PSS (\approx 150 °C), which could explain the enhancement in the aging rate relative to the BuNB-*r*-HFANB on silicon in the 1µm thick films. However, as the film thickness decreases, the aging rate is suppressed and there are cases where the aging on either PAA or PSS can lead to a reduced aging rate than the silicon control. The aging rate on the silicon decreases for BuNB-r-HFANB films that are less than 400 nm thick with approximately a factor of 2 decrease in β . For the films supported on PAA, the aging rate of the BuNB-r-HFANB is generally the fastest of the three substrates examined as might be expected with the proximity of T_g of the PAA to the aging temperature due to the decrease in modulus for glassy polymers on the approach to T_g and the influence of the modulus of the underlying layer on the T_g of the coating film.²⁷ However as the supporting layers are thin (ca. 2 nm), the thermal expansion of thin PAA and PSS was determined by ellipsometry (Figure S10), but there were multiple kinks in these curves similar to the multiple Tg's reported by Roth and coworkers for PS.⁶⁶ These correspond to approximately 120 °C and 155 °C for the PSS and 90 °C and 175 °C for the PAA.

The aging rate decreases precipitously between 50 nm ($\beta = 0.8 \times 10^{-3}$) and 150 nm ($\beta = 2.1 \times 10^{-3}$). The aging rate for the thinnest film examined on PAA is the slowest of any film in this study. The thickness dependence of aging on PSS is stronger than the silicon control with a decrease in aging rate for films as thick as 590 nm. However, the aging rate appears to plateau for films thinner than 230 nm. As shown in Figure 3, the aging behavior is dependent on the contacting polymer layer, but the thickness dependence suggests that the mobility of the adjacent polymer layer does not alone control the aging rate.



FIGURE 3. Impact of thickness on initial aging rate for BuNB-*r*-HFANB at 100 °C supported on (▲) clean silicon wafer, (●) 2 nm PAA film, and (■) 2 nm PSS film. There is a general trend for decreased aging rate for thinner films, but the thickness at which the aging is suppressed and the relative rate for the suppression in aging rate with decreasing thickness is dependent on the substrate. Dashed lines are provided as a guide for the reader's eyes.

The stress state of the polymer has been demonstrated to be a critical factor in determining the aging rate in polystyrene films.^{43,44} Thus, the differences in the initial aging rates may also be associated with the stresses developed in the film. Moreover, the evolution of the stress state during aging may be associated with the non-monotonic thickness during aging observed in some films. Wrinkles associated with buckling instabilities from these films after transfer to PDMS provide a route to determine the residual stress in these thin BuNBr-HFANB films. Figure 4 shows 3D optical micrographs of wrinkled ≈100 nm films that were supported on PSS at a constant (0.7 %) applied strain at different aging times. In all cases, periodic wrinkles can be observed that are associated with the mechanical mismatch between the BuNB-r-HFANB film and the PDMS substrate. These measurements only include the BuNB-r-HFANB as the PSS or PAA act as sacrificial film transfer layers that are dissolved in water during the transfer process to the PDMS.⁶⁷ The wavelength of the wrinkles, λ (peak to peak distance), can be directly related to the elastic modulus, while the amplitude, A (peak to valley height), can be related to the stress state of the film.⁶⁸ As shown in Figure 4A, the wrinkles of the as cast film are not well developed with the individual wrinkles being discontinuous. This leads to a broad distribution for the amplitude of the wrinkles. This behavior is dependent on the applied strain and the wrinkles become better resolved at higher strains (Figure S4). The wrinkles become better defined after aging for 30 min (Figure 4B) or 1 h (Figure 4C). The amplitude of the wrinkles appears to be more uniform in these cases. After additional aging (2h, Figure 4D), the quality of the wrinkle structure degrades slightly. The wrinkles are less uniform than typically reported for these mechanical measurements (see Figure S16 for wrinkled polystyrene using the same protocol). This can be partially attributed to the low strains applied due to the brittle nature of the BuNB-r-HFANB as cracks appear at relatively low strain (~1%). However in all cases, the periodic wrinkle structure can be resolved in order to assess the mechanical properties.



FIGURE 4. False color 3D optical micrographs of wrinkled \approx 100 nm BuNB-r-HFANB film at 0.7% applied strain for (A) as cast film (on PSS) and after (B) 30 min, (C) 1 h, and (D) 2 h of aging at 100 °C on PSS. The width of the micrographs is 1.2 mm. A line profile of across the surface is shown in the inset to better illustrate the periodic wrinkled structure. The profile is associated with the heights on the white line in the 3D image.

From these micrographs, the average amplitude and wavelength of the wrinkles are extracted in order to calculate the elastic modulus using equation 2 and residual stress using equations 4 and 5 for the BuNB-r-HFANB films as a function of physical aging. The thickness evolution during the aging of these films is shown in Figure S2. Figure 5 illustrates how the selection of the substrate (PSS and PAA) and film thickness impact the elastic modulus and residual strain of aged BuNB-r-HFANB films. The BuNB-r-HFANB was not cleanly removed from the bare silicon substrate after aging, so information about how the residual stress and elastic modulus changes during aging on the silicon could not be obtained. The elastic modulus appears to depend more on the film thickness than the underlying substrate as shown in Figure 5A. The thinner films (≈100 nm) in general exhibit a higher elastic modulus than the thicker films. Although the changes in the modulus during aging can be similar to the uncertainty in the modulus, there are some statistically significant differences during aging and trends in the average moduli that can provide insight into the unusual aging behavior of the BuNB-r-HFANB films.

Aging on PSS leads to a small increase in elastic modulus for both thicknesses at short aging time (≤ 60 min), but this increase in modulus is greater than one would expect with the limited densification of the films (Figure 2C). At 120 min of aging on PSS, the elastic modulus of the thinner (≈ 100 nm) film decreases – at a similar time point to where the aging does not further densify the film (Figure 2C and Figure S2D). The modulus for the thicker film does not change on further aging to 6 h, although the film expands during this time (Figure S3). Generally, the modulus is correlated with the density for polymers, but this correlation does not appear to hold for the BuNB-*r*-HFANB films during aging.

Aging on PAA leads to an initial increase in elastic modulus and then the modulus decreases as the aging continues. These results further indicate a decoupling between the specific volume



(thickness) and elastic modulus of the BuNB-r-HFANB during aging. For the thicker (≈200 nm) films on the PSS, the elastic modulus monotonically increases during the aging process as these films exhibit decreased expansion at long aging times in comparison to the thinner films. On PAA, the elastic modulus of the BuNB-r-HFANB films goes through a minimum during aging. These changes in modulus are not necessarily correlated with the thickness (volume) changes during aging, although the observed aging is known to be dependent on the specific property examined (e.g., enthalpy, modulus, volume) for bulk materials,³⁶ so decoupling of volume (thickness) and modulus in the aged samples is not unexpected.



FIGURE 5. Effect of physical aging at 100 °C on (A) elastic modulus and (B) residual stress of BuNB-*r*-HFANB film on (\bullet) PAA and (\blacksquare) PSS for \approx 100 nm (solid symbols) and \approx 200 nm (open symbols) films. In this case, the error bars on the data points are the standard error associated with the measurement.

Figure 5(B) shows how the residual stress in the BuNB-r-HFANB films evolves during physical aging at 100 °C. Irrespective of the thickness or supporting substrate, the residual stress was negative in the BuNB-r-HFANB film, which is indicative of a compressive strain. In the early stages of physical aging, the residual strain becomes more compressive as might be expected with the densification during aging. Except for the ≈ 100 nm film on PAA, the residual stress goes through a minimum after 1 h of aging. Due to the uncertainty associated with the wrinkling (Figure 4) like most mechanical measurements, the confidence in the statistical significance of the differences in the average properties is somewhat limited. The minimum in residual stress occurs at a shorter aging time for the ≈ 100 nm film on PAA. The change in the residual stress is greater for the ≈200 nm films than for the \approx 100 nm films. The residual stress does not appear to depend on the substrate (PSS or PAA). However, the minimum in stress appears to occur near the time associated with reversal in the aging behavior from densification to expansion. This correspondence provides some additional confidence in the differences reported in the average residual stresses in these films through the aging procedure.

In order to understand if the residual stress can be used to explain the differences in aging rates on the different substrates, the initial stress (which could be determined for the films on the bare silicon wafer) was used along with the film thickness to develop a scaling law relationship for the aging rate. Figure 6 illustrates the best collapse of the aging data for the BuNB-*r*-HFANB films. Although there is some scatter in the data, the aging rate appears to scale with the product of the film thickness and the critical strain by the following expression:

$$\beta = 2.9 \times 10^{-7} (h_o / \sigma^{1/3}) + 1 \times 10^{-3}$$
(8)

In comparing Figure 6 with Figure 2, there is clearly an improvement in the collapse of the data when including the residual stress state of the films. Although this scaling (eqn 8) is only an

emperical fit to the data, this correlation between the residual stress and aging rate agrees with the prior work of Roth and coworkers that examined how the stress state influenced the aging rate in free standing polystyrene films.⁴³ This work demonstrates that residual stress has a similar effect on the aging of supported films.



FIGURE 6. Empirical scaling of the aging rate with film thickness and critical strain.

CONCLUSIONS

Here, we explore the relationships between the aging and mechanical properties as a function of the substrate chemistry for films 50 nm to 1 µm thick of a high T_g polymer, BuNB-*r*-HFANB. For all substrates, the aging rate decreases as the film thickness decreases below a threshold value. This threshold thickness depends on the substrate: ≈500 nm on bare silicon, ≈900 nm on PAA, and ≈600 nm on PSS. In general, films on PAA age faster than films on silicon or PSS except For film for the thinnest films examined. thicknesses below ≈150 nm, unusual aging behavior was observed with the film thickness initially decreasing, but holding the film isothermally at 100 °C leads to an expansion in the film after some time. This time decreased as the film thickness decreased. The aging was found to influence the mechanical properties of the BuNB-r-HFANB films. Both elastic modulus and residual strain are not significantly impacted

by the substrate (PAA and PSS), but the elastic modulus did depend on film thickness. The aging rate for these films on different substrates were found to approximately scale with the product of the film thickness and residual strain to the -1/3 power.

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GRAPHICAL ABSTRACT

Effect of Adjacent Hydrophilic Polymer Thin Films on Physical Aging and Residual Stress in Thin Films of Poly(butylnorbornene-*ran*-hydroxyhexafluoroisopropyl norbornene)

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The residual stress in aged films were determined from wrinkling. Different polymer support layers led to changes in the observed aging rate, but the aging rate could be collapsed by scaling with thickness and residual stress.



Supporting Information

Effect of Adjacent Hydrophilic Polymer Thin Films on Physical Aging and Residual Stress in Thin Films of Poly(butyInorbornene-*ran*hydroxyhexafluoroisopropyl norbornene)

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Figure S1 shows the normalized film thickness as a function of aging time for two BuNB-r-HFANB films that were (115 to 120) nm thick on native silicon oxide. The films were aged at 100 °C for 17 h. Initially the film thickness decreases as expected, but after \approx 100 min of aging the film thickness begins to increase with additional aging time. This unusual aging behavior was found to be highly reproducible as shown in Figure S1.



FIGURE S1. Normalized film thickness as a function of aging time for (115 to 120) nm thick BuNB-r-HFANB films aged at 100 °C on silicon wafers with native oxide. The unusual aging behavior including increasing film thickness with time is reproducible for all films examined in duplicate.

Figure S2 shows representative fits of the initial aging rates for BuNB-r-HFANB films on the different substrates. The films were aged at 100 °C. The dashed lines in Figure S2 show the linear fit used to calculate aging rate for the different film thicknesses. The time over which the fit to determine the aging rate was performed was up to the point where the film thickness started to become invariant and the linear fit no longer well described the data.



FIGURE S2. Representative fits to the initial linear region used to determine the aging rates for BuNB-r-HFANB films that are approximately (A) 1000 nm, (B) 500 nm, (C) 250 nm, (D) 150 nm, (E) 80 nm, and (F) 50 nm.



Figure S3 shows how the normalized film thickness evolves with time for \approx 100 nm (Figure S3A) and \approx 200 nm (Figure S3B) thick films. There is good agreement in the aging behavior for the different total aging times examined: 0.5 h, 1 h, 2 h, and 6 h. These films were subsequently transferred to PDMS and wrinkled to obtain the Young's modulus and residual stress of these films at different aging conditions (Figure 5).



FIGURE S3. Normalized film thickness of BuNB-r-HFANB as a function of aging time for (A) \approx 100 nm and (B) \approx 180 nm thick films on \approx 2 nm thick (•) PSS or (•) PAA. These films were aged from 0.5 h to 6 h and were used for the residual stress and elastic modulus (Figure 5).

Figure S4 illustrates the initial emergence of wrinkles as the strain is increased on a 110nm as cast (0 h heating) BuNB-rHFANB film on 2 nm PSS. Small wrinkles first appear at 0.05% strain for this film. Additional strain leads to an increase in the amplitude of the wrinkles. From these images, wrinkle amplitude and wavelength were determined to obtain the elastic modulus and residual stress in this film.



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Figure S4. False color 3D optical images of 110 nm thick, as cast (0 h heating) BuNB-rHFANB film on 2 nm PSS film after transfer to PDMS. The applied strain is progressively increased from (A) 0% to (B) 0.055% strain, (C) 0.07% strain, (D) 0.08% strain, (E) 0.10% strain, (F) 0.12% strain, (G) 0.13% strain, and (H) 0.15% strain.



This series of images was used to obtain the average wrinkle amplitude as a function of the applied strain. As shown in Figure S5, the wrinkle amplitude increases with increasing strain, but the amplitude depends on the aging history and the substrate chemistry (PAA vs PSS). The residual strain in the films was calculated via equation 4. The average residual strain from the different applied strains is reported for the different aging times.



FIGURE S5. Average wrinkle amplitude as a function of applied strain for ≈100 nm film on (A) PAA and (B) PSS and ≈180 nm films on (C) PAA and (D) PSS for BuNB-r-HFANB films. The amplitude is dependent on the aging of the film.

(A) BuNB-r-HFANB on Silicon

-	Layer # 3 = <u>Cauchy</u> Thickness # 3 = <u>114.43 nm</u> (fit)			
	A = <u>1.458</u> (fit) B = <u>0.00555</u> (fit) C = <u>-8.5096E-05</u> (fit)			
	k Amplitude = <u>0.00236</u> (fit) Exponent = <u>0.512</u> (fit)			
	Band Edge = <u>400.0 nm</u>			
	Layer # 2 = <u>SIO2_JAW</u> Oxide Thickness = <u>1.00 nm</u>			
	Layer # 1 = <u>INTR_JAW</u> Interface Thickness = <u>0.70 nm</u>			
÷	Substrate = Si Temp (Temp Library)			

(B) PSS on Silicon

-	Layer # 3 = <u>Cauchy</u> Thickness # 3 = <u>4.87 nm</u> (fit)					
	A = <u>1.412</u> (fit) B = <u>0.05691</u> (fit) C = <u>0.0000</u>					
	k Amplitude = <u>1.01338</u> Exponent = <u>0.153</u>					
	Band Edge = <u>400.0 nm</u>					
	Layer # 2 = <u>SIO2_JAW</u> Oxide Thickness = <u>1.00 nm</u>					
	Layer # 1 = <u>INTR_JAW</u> Interface Thickness = <u>0.70 nm</u>					
÷	Substrate = <u>Si Temp (Temp Library)</u>					

(C) BuNB-r-HFANB on PSS (layer 3)

-	Layer # 4 = <u>Cauchy</u> Thickness # 4 = <u>174.21 nm</u> (fit)
	A = <u>1.492</u> (fit) B = <u>0.00149</u> (fit) C = <u>0.0000</u>
	k Amplitude = 0.0000 Exponent = 0.00
	Band Edge = <u>400.0 nm</u>
+	Layer # 3 = <u>Cauchy</u> Thickness # 3 = <u>2.10 nm</u>
	Layer # 2 = <u>SIO2_JAW</u> Oxide Thickness = <u>1.00 nm</u>
	Layer # 1 = <u>INTR_JAW</u> Interface Thickness = <u>0.70 nm</u>
+	Substrate = <u>Si Temp (Temp Library)</u>

Figure S6. Model in CompleteEase software (J.A. Woollam) used to fit the ellipsometric data. Examples for the different substrates are shown: (A) 115nm BuNB-r-HFANB on silicon, (B) PSS on silicon, and (C) 175nm BuNB-r-HFANB on 2nm PSS.

Figure S6 shows the model used to fit the ellipsometric angles, psi and delta, to determine the film thickness and refractive index using the Complete Ease software. Figure S6A shows an example of the model used to fit ellipsometric data for a BuNB-r-HFANB film on silicon with an example film thickness of 115nm. The substrate included the standard temperature dependent silicon layer that couples directly with the measured temperature on the heat stage. The silicon is optically thick, so 1mm is arbitrarily thicker than the optical pathlength. Above the silicon layer, an intermix layer between the silicon and silicon dioxide with an interface thickness of 0.7nm is used as this has been demonstrated to improve the fits for native oxides¹ with an additional silicon dioxide layer that is 1nm thick. This model for the silicon



and the native oxide has been confirmed using cleaned silicon wafers. The BuNB-r-HFANB is represented by a Cauchy layer to characterize its optical properties. The Cauchy equation is:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$
(1)

where A, B, and C are the Cauchy coefficients to describe the wavelength dependence of the refractive index. For the BuNB-r-HFA-NB film in this case, the coefficients were A = 1.458 and B = 0.00055. C was set to zero as it was not necessary to fit these ellipsometric data. This fit results in a refractive index n@632nm = 1.47 and MSE (mean squared error) = 3.31 over the full wavelength range examined. The same general model was used for all BuNB-r-HFANB films on silicon.

Figure S6B shows the ellipsometric model for a ~5nm PSS layer on silicon. The PSS is fit with a Cauchy model. The film thickness and optical constants for the PSS layer are then fixed for the subsequent processing where the PSS is coated by a BuNB-r-HFANB film. Figure S6C shows the ellipsometric model for a BuNB-r-HFANB film deposited on a thin PSS layer. In this model, layer #3 represents the PSS film and layer # 4 represents the BuNB-r-HFANB film. The only fit parameters in this case are A and B for the Cauchy layer associated with the BuNB-r-HFANB film and the thickness of this film. The identical model approach developed for the PSS was used for the PAA.



Figure S7: The measured (solid) and fit (dashed) ellipsometric angles, psi and delta, for 115nm thick film of BuNB-r-HFANB on silicon that were aged at 100 °C. (A) t = 0 min, (B) t = 10 min, (C) t = 500 min, and (D) t = 1000 min.

Figure S7 shows the ellipsometric angles for a 115nm BuNB-r-HFANB film on silicon for films that were aged at 100°C. Figure S7A shows the experimental psi and delta and model fits for the initial film prior to aging. Figure S7B shows the same curves but at t = 10min of aging. Figure S7C s shows the same curves but at t = 500 min of aging. Figure S7D shows the data at t = 1000 min. In all cases, the data are well fit by the model.





Figure S8: Refractive index of BuNB-r-HFANB films at 632nm for the as cast film on 2nm PAA (■), 2nm PSS (▲), or on silicon (●) as a function of film thickness. There is no significant variation in the refractive index

Figures S8 shows the refractive index as a function of film thickness for BuNB-r-HFANB film on PAA, PSS, and silicon. The error bars represent the standard error of measurement. The refractive index does not vary significantly for the three substrates, nor with film thickness.



Figure S9. Isothermal heating of BuNB-r-HFANB film on silicon at 200°C for 72 h. (A) film thickness vs time for heated film, (B) normalized film thickness vs time for heated film where black dashed line indicates the aging rates of the 900nm BuNB-r-HFANB film on silicon at 100°C. (C) FTIR spectra of a BuNB-r-HFANB film before (blue) and after (red) heating at 200°C.

Figure S9 shows the unusual aging behavior of a 900nm BuNB-r-HFANB film at 200°C for 72 h. As shown in Figure S9A, the film thickness initially decreases slightly from h(10min) = 895nm to h(100min) = 881nm. After 100min of aging, film thickness decreases at a much faster rate to a final thickness, h(2797min) = 638nm, that is nearly 30% less than the initial thickness. This is better illustrated in Figure S9B by the normalized film thickness versus time where the black dashed line shows the aging rate of a 900nm BuNB-r-HFNAB at 100°C. To explain the large decrease in thickness, the chemistry of the film was examined before and after aging with FTIR. Figure S9C shows the FTIR data for a BuNB-r-HFANB film that has been aged at 200°C. A new peak around 1700 1/cm appears after aging, which corresponds to the development of a new C=O bond. Thus, the polymer is degrading even at 200°C, so degradation would be an issue for annealing the BuNB-r-HFANB film above its glass transition temperature of 350°C prior to aging experiments.



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Figure S10. Temperature sweeps of thin PAA and PSS film to determine their T_g . Temporal changes in Psi at incident angle of 70° for (A) 2nm PSS film and (B) PAA film on heating from 30°C to 190°C at 2°C/min. (C) The normalized product of the refractive index and film thickess (nh/nh@30°C) for the two films. The refractive index used is n@632nm.

Temperature sweeps on heating were used to determine the glass transition temperature of the thin PSS and PAA film. The thin films were heated from room temperature to 190°C at a heating rate of 2°C/min. Figure S10A and S10B show the curves associated with the ellipsometric angle, psi, for the heating process of the 2nm PSS and 2nm PAA film for select wavelengths where the colored lines are the measured psi data and the black dashed lines are the fits.. Due to coupling of n and thickness for such thin films, their product is used to examine the temperature dependent properties of the PAA and PSS thin films. Figure S6C shows the (nh)/(nh @ 30°C) vs temperature for the PSS and PAA films. There are multiple kinks in the curves that could be associated with Tg's for these materials.



Figure S11: Aging of ~150 nm BuNB-r-HFANB films on PAA, PSS, and silicon. (A) Normalized film thickness vs time for the aging between 10min – 20min. (B) Normalized film thickness vs time for the full aging time. (C) The aging rate is not strongly dependent on the selection of the time for h_0 : 10min, 15min, and 20min.

A time point of $h_o = 10$ min has been used for aging rates but the time point chosen is arbitrary. Figure S11 shows the aging of ~150 nm BuNB-r-HFANB films on PAA, PSS, and silicon. In S11A between 10min and 20min, the film thickness decreases linearly with time as expected. Figure S11B shows the entire aging behavior. The table in Figure S11C shows the aging rates calculated using different h_0 values of 10min, 15min, and 20min based on equation (1) from the text. Changing h_0 will alter the normalization slightly but not impact the calculated aging rate.



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Figure S12: (A) Film thickness and refractive index as a function of time for BuNB-r-HFANB film on silicon swelled in toluene vapor at $P/P_0 = 0.15$. (B) Void volume fraction as calculated from the Bruggeman effective media approximation based on the refractive index change and the film swelling.

As the BuNB-r-HFANB films were not annealed above T_g , vitrification during film formation could lead to significant porosity in the films. To quantify any porosity, a nominal 390nm film was swollen in toluene vapor and the film thickness and refractive index change was measured. The BuNB-r-HFANB film was placed within a homemade ellipsometric porosity cell that allowed solvent vapor flow while simultaneous measurement ellipsometric properties.² Figure S12A shows the film thickness and refractive index change of the BuNB-r-HFANB film in the toluene vapor over the course of the experiment. The film thickness increased from 389nm to 396nm, while the refractive index increased from 1.464 to 1.4705. An effective medium approximation approach was used to determine the void fraction based on ideal mixing ($\Delta V^{EX} = 0$) following the procedure developed by Silverstein and coworkers.^{3,4} Figure S12B shows the volume percent of voids within the BuNB-r-HFANB film. The BuNB-r-HFANB film has ~ 3% voids in the films based on the ideal mixing. However, sorption of gases within glassy polymers are known to first fill free volume through the dual mode sorption,⁵ so this void fraction determination also includes the intrinsic free volume of the polymer.



(1)		500nm scan		2um scan	
		Ra (nm)	Rq (nm)	Ra (nm)	Rq (nm)
125nm	as cast	0.147	0.816	0.268	0.212



	aged	0.187	0.149	0.255	0.203
270nm	as cast	0.183	0.146	0.264	0.21
3701111	aged	0.197	0.157	0.277	0.219

Figure S13: AFM images of spin coated BuNB-r-HFANB for as cast and aged films for ~125nm and ~370nm films for a 500nm x 500nm scan size and a 2μm x 2μm scan size to determine surfouce roughness. (A) 125nm as cast film, 500nm scan size, (B) 125nm as cast film, 2μm scan size, (C) 125nm aged film, 500nm scan size, (D) 125nm aged film, 2μm scan size, (E) 370nm as cast film , 500nm scan size, (G) 370nm aged film, 500nm scan size, (H) 370nm aged film, 2μm scan size, (H) 370nm aged film, 2μm scan size, (I) roughness values for AFM images. Films were aged for 17hr at 100°C.



Figure S14. The effect of soaking thin PSS and PAA films in a THF/toluene mixture overnight and then drying in a vacuum to remove any solvent from the. (A) shows the ellipsometric psi curves of the PSS films before and after solvent soaking, (B) the ellipsometric psi curves of PAA film before and after solvent soaking, and (C) the film thickness of the PSS and PAA film before and after soaking in THF/toluene mixture overnight. There is no dissolution of either polymer by the THF/toluene. The thickness is invariant within the uncertainty of the measurement.



Figure S15. BuNB-r-HFANB films on silicon do not age when held at room temperature. (A) shows the psi curves at incident angles of 65°, 70°, and 75° for a ~125nm BuNB-r-HFANB that was left at room temperature for one week where the solid colored curves are the initial as cast films and the black dashed curves as the psi curves after one week. (B) Shows the psi curves for a ~380nm BuNB-R-HFANB with the same conditions. (C) shows the film thickness before and after one week at 22°C.

BuNB-r-HFANB films do not change in film thickness when held at room temperature, under ambient conditions as described by Figure S15. This figure shows a 125nm and a 370nm BuNB-r-HFANB film on silicon left a room temperature, 22°C, under ambient conditions, for one week. Figure S15A shows the psi curves for the 125nm for measurement angles of 65°, 70°, and 75° for the initial film measurements and after the films had been left for a week where the solid colored curves represent the initial measurements and the black dashed lines are the curves after one week. We can see that the curves before and after one-week line up with one another indicating that optical properties and film thickness has not changed for the film over the course of a week's time. S15B shows the similar psi curves for a 380nm BuNB-r-HFANB film again left over the course of a week where again the colored curves represent the initial measurement and the black dashed curves represents the measurement after one week. Again, we see the measurement after one week lies up with the initial film implies that optical properties of the BuNB-r-HFANB film has not changed. Figure S15C shows the film thickness for the BuNB-r-HFANB films initially and after one week. We can see that for the thinner film, initially we have a film thickness of 124.3nm and after one week a film thickness of 124.9nm. Considering the error associated with these measurements, there is no change in film thickness after one week at ambient conditions. The same this is true for the thicker film, with an initial film thickness of 369.9nm to 370.4nm after one week.



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Youngs Modulus	3.21 GPa
Critical Strain	0.018

Figure S16. Defined wrinkles of as cast 104nm polystyrene film at 0.01 applied strain using the same PDMS and transfer procedure as for the BuNB-r-HFANB. The corresponding Young's modulus and critical strain are included.

Approximately 400kg/mol polystyrene was used to spin coat a 104nm film that was wrinkled following the same procedure as the BuNB-r-HFANB films. Figure S16 shows an image of the wrinkled film with the nice periodic wrinkles. The calculated modulus was 3.21GPa with a critical strain of 0.018 which agrees with prior reports.^{6,7}



Figure S17: Normalized film thickness as a function of aging time of BuNB-r-HFANB on 2nm PSS for films between 45nm and 980nm at 100°C for 17h.

Figure S17 shows the thickness dependence of the aging of BuNB-r-HFANB films on 2nm PSS at 100°C. This graph is a repeat of Figure 2C in the manuscript to show the full range of the aging of a 45nm BuNB-r-HFANB film on PSS where no film decrease is seen, only film expansion. In general, for the data shown in Figure S17, for thick film we see constants decrease in film thickness with time. Film expansion occurred in films as thick as 230nm.

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