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Influence of Chain Stiffness on Thermal and Mechanical Properties of Polymer Thin Films

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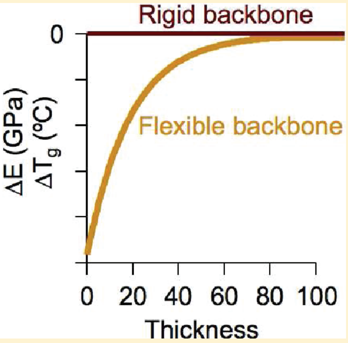
S *Supporting Information*

ABSTRACT: The effect of main chain stiffness and side chain flexibility on the elastic modulus and glass transition temperature (T_g) of thin polymer films is investigated using nontraditional polymers formed from 5-(2-phenylethylnorbornene). Depending on the polymerization route chosen, the resulting polymer backbone is comprised of either bicyclic (norbornyl) units, which leads to a relatively rigid polymer with a high bulk T_g, or monocyclic (cyclopentyl) units, which leads to a more flexible structure with a lower bulk T_g. The modulus and T_g of the rigid bicyclic polymer are thickness independent down to <10 nm, whereas the modulus of the more flexible monocyclic polymer decreases with decreasing thickness. By hydrogenation of the pendant phenyl ring to the cyclohexyl counterpart, we illustrate that minor changes in the relative flexibility of the side chain do not impact the observed thin film behavior. To further support our hypothesis that main chain stiffness (persistence length) plays a central role in confinement-induced changes in physical properties, a series of arylate/phosphonate copolymers, where the addition of phosphonate groups decreases the overall stiffness of the polymer backbone, are also examined. Similar to the polynorbornenes, the poly(arylate-*co*-phosphonate) polymers exhibit more pronounced thickness-dependent properties as the stiffness of the backbone decreases. We believe based upon our results that examination of chain flexibility in the thin film glass community for future works would be extremely useful in elucidating the physical origins of observed phenomena.



INTRODUCTION

One outstanding issue in fundamental physics is understanding of the glass transition.[1−3] Over the past decades, there has been a concerted effort in examining how the glass transition temperature (T_g) changes with confinement of the glass former to nanoscale dimensions.[4,5] In particular, a single polymer, polystyrene (PS), has been examined extensively to assess how confinement to thin films impacts its physical properties including T_g,[6−9] thermal expansion,[8,10] elastic modulus,[11] chain conformation,[12] segmental motion,[13,14] viscoelasticity,[15] and creep behavior,[16] as examples. However, these studies have yielded conflicting conclusions depending upon the technique used. For example, T_g of supported ultrathin PS films has been shown to decrease when using fluorescence,[7,17] Brillouin light scattering,[18] or ellipsometry,[19] but microcalorimetry[20] indicates no change in T_g irrespective of thickness. Russell and co-workers have recently suggested that the observed changes in T_g for confined thin films is a result of residual stress and not intrinsic changes in the physical properties,[21] which is similar to conclusions by Kremer and co-workers based upon long-term annealing of polymer thin films.[22] Even if the thickness-dependent properties of these polymer films are indeed artifacts of the film formation process, it will not always be possible to anneal out these effects in technological applications due to the time associated with the chain relaxation. For example in microelectronics, lithographically patterning the surface of polymer thin films leads to a decrease of T_g, which is attributed to increasing the area of the free surface.[23] These discrepancies in the conclusions provide motivation to examine the thin film behavior in greater detail.

One route to improved understanding of the glass transition upon confinement is to examine polymers other than PS. For example, by utilizing poly(methyl methacrylate) (PMMA) with different tacticities, it was shown that the specific monomer interaction with the substrate can dramatically impact the observed thickness-dependent

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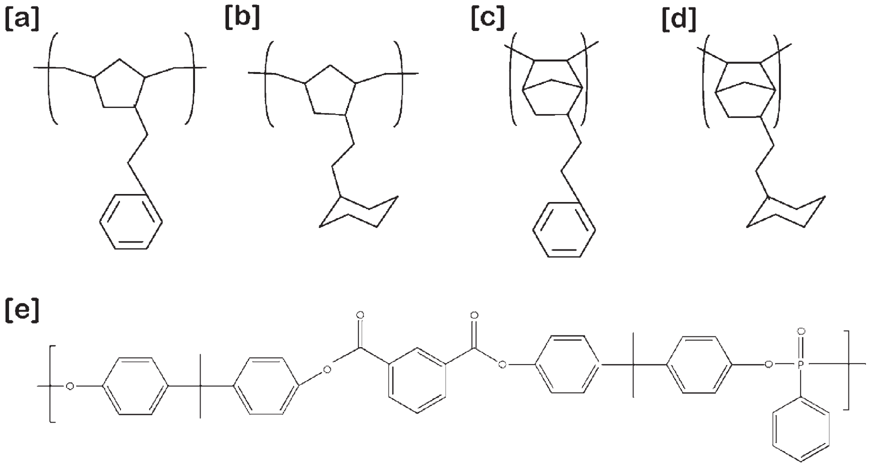

Figure 1. Structure of the poly[5-(2-phenylethylnorbornene)]s: [a] hROMP PENb, [b] hROMP CENb, [c] Add PENb, [d] Add CENb, and [e] arylate−phosphate copolymer.

behavior.[24,25] The homologous series of poly(*n*-alkyl methacrylate)s provides a facile route to examine how polymer structure impacts thin film behavior.[26] In this case, there appears to be some correlation between cooperative dynamics in the bulk and the thin film behavior.[27,26] Similarly, Ellison and Torkelson examined how minor variations to the monomer structure of PS impact the thin film behavior,[7] but no obvious correlation between cooperative motion and T_g changes was observed.

Additionally, the incorporation of diluents into the polymer appears to eliminate the influence of confinement on both T_g[28,29] and modulus[30] of polymer thin films. Even with the addition of solvents, there are contradictions in the literature; using a bubble rheometer, the creep behavior of thin films scales as expected with the addition of a plasticizer.[16] However, in most cases, relatively flexible polymers have been examined. When considering polymer chain flexibility, both the chemical structure of the polymer (i.e., conjugation and aromaticity in backbone) and conformational limitations due to steric hindrances must be considered. For example, commercial polycarbonate (PC) is more flexible than PS despite the aromaticity in the backbone due to the steric hindrance of the pendant phenyl group in PS. Soles and co-workers reported a depression in T_g for thin films of PC using X-ray reflectivity and positron annihilation lifetime spectroscopy,[31] but the segmental dynamics of PC appear to be suppressed upon confinement.[32] Torkelson and co-workers have in a separate effort reported that PC is more susceptible to confinement effects than PS, which has been attributed the requirements for cooperativity of segmental mobility.[33] McKenna and co-workers reported a dramatic decrease in T_g for free-standing PC films.[34] These results appear to be counter to those obtained generally for PS where T_g is significantly decreased and the segmental dynamics are enhanced in ultrathin films.[13,35] Thus, a more detailed examination of monomer-specific effects could provide insight into critical parameters that control deviations in physical properties for thin film glasses.

There are several potential routes in polymer science to systematically vary the physical properties of a polymer series such as through a combination of short-chain branching and long-chain branching to the polymer backbone to impact the entanglements and steric hindrance,[36] via copolymerization, which can tailor the fire-resistant behavior of polyarylates as an example,[37−39] or postpolymerization modification, such as selective hydrogenation of unsaturated bonds.[40−43] We will utilize the latter two techniques to probe chain stiffness systematically.

As the conformation of polymer chains is primarily controlled by torsion about individual bonds,[44] small alterations in the atomic structure of the polymer backbone can dramatically impact the chain stiffness. In this paper, the backbone rigidity of a 5-(2-phenylethylnorbornene) polymer (PENb) is varied by polymerization route, where addition polymerization leads to a bicyclic (norbonyl) ring in the polymer backbone limiting the chains conformation due to hindered torsional rotation and ring opening metathesis polymerization generates a monocyclic (cyclopentyl) polymer backbone that increases the number of available molecular conformations as backbone flexibility is increased.[45] Further modification by saturation of the pendant phenyl ring allows for systematic variations in side chain flexibility with no impact on backbone flexibility. Saturation of the phenyl ring to a cyclohexyl moiety should lead to decreased side chain flexibility due to increased steric hindrance, similar to the systematic increases in persistence length of PMMA with the addition of bulky side groups.[46,47] To further test the impact of backbone rigidity on thin film properties, a series of arylate−phosphonate copolymers produced by polycondensation of bisphenol A (BPA) with phenylphosphonic dichloride (PPDC) and isophthaloyl chloride (IPC) are also examined,[38] where addition of phosphonate groups decreases the overall stiffness of the polymer backbone. These two systems of polymers provide a facile route to examine the impact of subtle changes in the polymer backbone and/or pendant groups on the physical properties of confined polymer glasses. The thickness dependences of both mechanical and thermal properties of these polymers are examined using surface wrinkling[48] and ellipsometry. We find that polymers with stiffer backbones exhibit limited changes in T_g and elastic modulus for thin films, while those with more flexible backbones exhibit thickness-dependent properties similar to those for PS[6] and PMMA.[49]

■ EXPERIMENTAL SECTION

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.

Silicon wafers (450 μm thick) were used as substrates; the wafers were cut into approximately 3.5 cm × 3.5 cm pieces and cleaned with ultraviolet-ozone (model 42, Jelight) for 40 min. Poly(styrenesulfonic acid) (PSS) was utilized as a release layer to enable surface wrinkling on PDMS. PSS in 2-propanol solution was spin-cast onto the cleaned wafers. The film was annealed in vacuum at 130 °C for 24 h in order to remove the remaining solvent. After annealing, the film thickness and optical constants for the PSS layer were determined using a variable angle spectroscopic ellipsometer (VASE, J.A. Woollam Co., Inc.). Measurements were performed from 40° to 75° in 5° increments and fit using a Cauchy model.

Aryl−phosphonate copolymers were synthesized as reported previously.[38] These copolymers were dissolved in anhydrous dimethylformamide and then spin-coated onto the PSS-coated or ultraviolet/ozone-cleaned silicon wafers for modulus and T_g measurements, respectively. The four poly[5-(2-phenylethylnorbornene)] derivatives reported previously[45] (hROMP PENb, hROMP CENb, Add PENb, and Add CENb) were dissolved in toluene and then spin-coated to form the films. The structure for each of these polymers is shown in Figure 1. Variations in both solution concentration and spin speed allowed for systematic reduction in film thickness. After spin-coating the samples, the films were annealed at 200 °C for 24 h in an inert N_2 atmosphere. The thickness of the polymer film was also determined using VASE and fit using a Cauchy model (and the previously determined optical constants and film thickness for PSS for the mechanical measurements).

To wrinkle the polymers to elucidate the elastic modulus, polydimethylsiloxane (PDMS) (Sylgard 184, Dow Corning) was utilized as the substrate and prepared at a ratio of 20:1 by mass of base to curing agent to a thickness of ~1.5 mm. The PDMS was allowed to degas at ambient for 3 h prior to curing at 100 °C for 2 h. Slabs of PDMS measuring 2.5 × 7.5 × 1.5 mm^3 were utilized as substrates for the wrinkling experiments. The bulk modulus of the PDMS was determined using a Texture Analyzer (TA.XT Plus, Texture Technologies). For the surface wrinkling measurements, the PDMS slab was mounted onto a custom built strain stage, prestrained to ≈3.5%, and then the polymer film of interest is transferred onto the prestrained PDMS.[25] The transfer was accomplished by placing the supported film in contact with the PDMS and immersing the system in a water bath. The polymer film transferred onto the PDMS surface, while the PSS layer dissolved in the water bath. The thickness of the transferred polymer film was measured for a second time utilizing ellipsometry in order to verify the complete transfer of the film and removal of the PSS. The film thickness obtained after transfer was in good agreement (within 10 Å) with that prior to transfer. In order to wrinkle the films, the prestrain on the PDMS was released at a rate of 0.1 mm/s at ambient temperature ($T = 21 \pm 2$ °C).

Characterization of the wrinkled surface was performed using atomic force microscopy (AFM, Agilent 5500) in intermittent contact mode using a constant scan size of 10 μm by 10 μm and optical microscopy (OM, Mititoyo Ultraplan FS-110) with an image resolution of 1024 pixels × 768 pixels. Both images were analyzed using a 1-D fast Fourier transform (FFT) in order to obtain the wavelength of the wrinkles.

The glass transition temperature (T_g) and coefficient of thermal expansion (CTE) of the polymer films directly cast onto the silicon wafer were measured using spectroscopic ellipsometry. The thermal response of the polymer was measured under a nitrogen atmosphere upon cooing from either 260 or 180 °C (for the PENb and copolymers respectively) to 30 °C at 1.0 °C/min. To determine the T_g of the film, the data were fit to the following empirical expression[6]

$$h(t) = w\left(\frac{M-G}{2}\right)\ln\left(\cosh\left(\frac{T-T_g}{w}\right)\right) + (T-T_g)\left(\frac{M+G}{2}\right) + c$$

where h is the film thickness, M and G are the linear thermal expansion coefficients of the melt and glass, w is the width of the transition, and c is the film thickness at $T = T_g$. In all cases, the error bars represent one standard deviation of the data, which is taken as the experimental uncertainty of the measurement. Representative curves from the ellipsometry data are available in the Supporting Information.

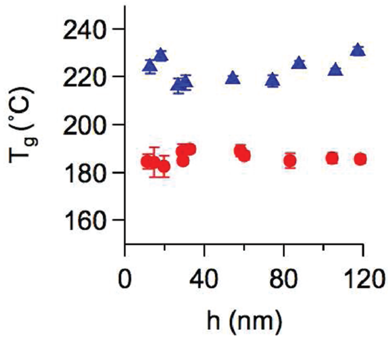

Figure 2. T_g as a function of film thickness for Add PENb (●) and Add CENb (▲).

RESULTS

The thermal behavior of the PENb-based polymers is examined by *in situ* ellipsometry to provide the temperature dependence on the film thickness and refractive index. For Add PENb and Add CENb, two distinct coefficients of thermal expansion (CTE) can be seen from the temperature-dependent thickness; the thickness dependence of the CTE in both the rubbery and glass regime is included in the Supporting Information. The T_g of these films is determined from the discontinuity in the thermal expansion. As shown in Figure 2, Add PENb films exhibit a T_g of 186.3 ± 3.7 °C that is statistically independent of film thickness; similarly, there is no thickness dependence to the T_g of Add CENb (223.1 ± 5.4 °C). This increase in T_g upon saturation of the pendent phenyl ring is consistent with previously reported data for these polymers determined via thermo-optical analysis (TOA).[47] However, there is an offset in T_g by ~27 °C between TOA and ellipsometric dilatometry; we have further examined this behavior with modulated DSC, where the T_g is found to agree with the ellipsometric measurements reported here. It is currently unclear why TOA provides such a large offset in T_g for these addition polymers. Nonetheless, this increase in T_g with saturation is consistent with the results for polyindene, which also has a backbone consisting entirely of cyclopentyl rings; saturating the fused phenyl ring to yield hydrogenated polyindene increases the bulk T_g by 60 °C.[42] In this case, the change in T_g is attributed to a reduction in main chain cooperative motion due to the conversion of the phenyl ring into a cyclohexyl moiety, which is supported by the decrease in density with saturation.[45] Interestingly, the T_g for these materials remains statistically invariant over all thicknesses examined from 120 nm down to less than 10 nm. As a comparison, PS, which has a pendent phenyl ring similar to Add PENb, exhibits a large decrease in T_g at thicknesses less than 30 nm from ellipsometry measurements[7] when not subjected to rigorous annealing.[22] Hydrogenation of the phenyl ring (to Add CENb) does not significantly impact the thin film behavior. The effect of backbone rigidity can be investigated by comparing these addition polymers (Add PENb and Add CENb) with the analogous polymers synthesized by ROMP and subsequent hydrogenation

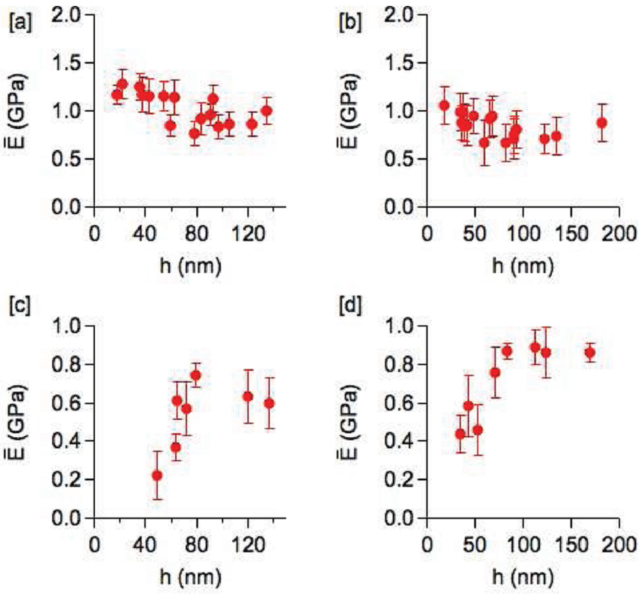

Figure 3. Modulus as a function of film thickness for [a] Add PENb, [b] Add CENb, [c] hROMP PENb, and [d] hROMP CENb.

(hROMP PENb and hROMP CENb). Unfortunately, the low T_g of these hROMP polymers prohibits the accurate identification of the glass transition by ellipsometry without an active cooling stage. However, other physical properties of these polymers can be examined to compare their thin film behavior.

Figure 3 shows how the room temperature modulus of each PENb-based polymer is impacted by film thickness. For Add PENb and Add CENb, the modulus of these materials is thickness independent, similar to the T_g behavior discussed previously. The modulus for the Add PENb polymer is approximately 1.0 ± 0.2 GPa from 140 nm down to 15 nm. The average modulus is slightly decreased to 0.88 ± 0.19 GPa with saturation of the phenyl ring into cyclohexyl (Add CENb), but this modulus is also thickness independent. These values are considerably less than observed for many common polymer glasses such as PS and PMMA (3−4 GPa); however, it should be noted that the modulus of other phenyl-substituted norbornenes (from addition polymerization) tend to be in the rangle of 2 GPa as measured by traditional DMA.[50] For an analogous addition PENb the modulus of the bulk PENb is 1.37 ± 0.20 GPa, which is on average greater than that of the thin film but within the uncertainty of both measurements. Irrespective, the moduli for these Add PENb and CENb films are suspiciously low compared to the bulk; one potential explanation would be preferential chain orientation in the plane of the film due to their relatively rigid backbone during film formation. In this case, the wrinkling would be primarily probing the mechanical response through the thickness of the film (perpendicular to chain orientation direction), which is counter to a bulk tensile test that measures stress/strain associated with deformations in the chain alignment direction. Studies on highly aligned systems have shown that $E_{\|}$ can be more than double $E_{\perp}$.[51] Additional work is required to fully understand why the elastic moduli for these two polymers are so low in the films; however, this change is not dependent upon the film thickness from 5 to 200 nm. In contrast to the T_g for the addition polymers, the modulus of the Add polymers actually decreased with saturation of the phenyl ring, which is unexpected from the perspective of density and T_g. However, there are differences in the specific interactions present that could impact the mechanical behavior; in particular, the phenyl rings provide a route for $\pi-\pi$ interactions that would not be present for the cyclohexyl containing polymer. Examining the data carefully, there appears to be a potential increase in modulus of the thinnest films. An increase in modulus has been reported previously for PMMA surfaces[52] and ultrathin films of PS appear stiffer from bubble rheology.[16] The increase in modulus observed here is within the uncertainty of the measurement and is significantly less than either of these prior studies. Nonetheless, both T_g and modulus are statistically independent of film thickness for both addition polymers.

In contrast to the addition polymers, the ring-opened PENb-based polymers exhibit a pronounced thickness dependence to the observed modulus as shown in Figure 3c,d. hROMP PENb with preserved phenyl ring has a modulus of 0.64 ± 0.11 GPa for films thicker than 80 nm; a 65% decrease in modulus to 0.22 ± 0.13 GPa occurs when the thickness is decreased to 42 nm. This decrease in modulus occurs at larger thicknesses than typically observed for PS,[11] but we have found that the length scale at which deviations in modulus occurs in thin polymer films scales inversely with the quench depth into the bulk glass.[53,54] As the measurement temperature approaches T_g, the modulus tends to begin to decrease in thicker films. The bulk T_g for hROMP PENb and hROMP CENb is reported to be 28 and 26 °C, respectively.[45] Based on previous examination of the thin film moduli of flexible styrene and methacrylate polymers,[53,54] a decrease in the modulus of hROMP CENb and hROMP PENb would be expected at ≈80 nm due to their relatively low bulk T_g; this is consistent with experimental observations. Interestingly, the hROMP CENb exhibits an increased modulus for films thicker than 80 nm (0.87 ± 0.10 GPa) and (33%) decrease in modulus to 0.58 ± 0.13 GPa at 41 nm. The modulus behavior of these hROMP polymers agrees qualitatively with previous results for flexible polymers, but to explain the behavior of the Add PENb and Add CENb thin films, a more detailed examination of other physical properties must be undertaken. We hypothesize that the stiffer polymer backbone of the addition polymers, which have no flexible spacers separating the alicylic rings, is responsible for the change in behavior. We have quantified the relative stiffness difference between Add CENb and ROMP CENb by examining the small-angle X-ray scattering of dilute toluene solutions; as the X-ray contrast is low, the persistence length could only be roughly estimated to be 2.9 and 1.8 nm for Add CENb and ROMP CENb, respectively. The persistence length for the ROMP CENb is very similar to that for PS;[55] there is quantitative agreement in the fractional decrease in the modulus for oligo-PS (same T_g) and ROMP CENb thin films from our wrinkling measurements.[53]

To further examine the role of chain stiffness on thin film behavior, a series of copolymers based on bisphenol A (BPA) with varying ratios of phenylphosphonic (PPDC) and isophthaloyl chloride (IPC) are examined. Figure 4 illustrates how T_g as a function of film thickness is dependent upon the aryl:phosphonate ratio in the copolymer. The T_g for thick films is increased as the phosphonate (PPDC) content in the copolymer is decreased. For the polymer that consists fully of BPA and PPDC, T_g is approximately 116.8 ± 1.8 °C from 100 nm down to 21 nm but then rapidly decreases for films less than 20 nm thick to 107 ± 0.5 °C for a 14 nm thick film. As the IPC:PPDC ratio is increased to 50:50, the bulklike T_g is increased to 132.5 ± 3.5 °C, but also the glass transition temperature begins to decrease at 40 nm with

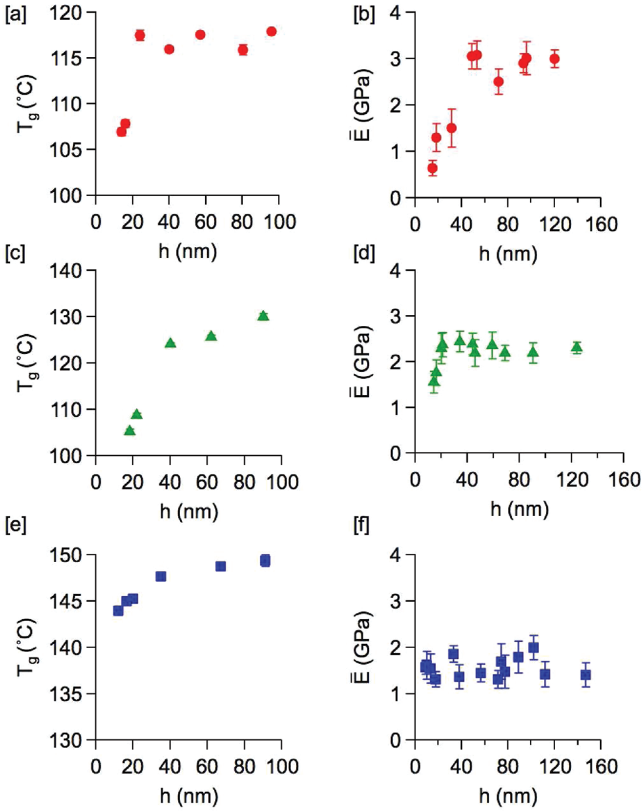

Figure 4. T_g as a function of film thickness and modulus as a function of film thickness for aryl−phosphonate copolymers with IPC:PPDC ratios of 0:100 (a, b), 50:50 (c, d), and 80:20 (e, f).

a decrease to 107.5 ± 1.2 °C at 18 nm observed. The highest T_g is observed for the 80:20 IPC:PPDC copolymer with a value of 150.7 ± 2.2 °C for the thickest films and only a slight decrease to 144.5 ± 0.45 °C at 12 nm. This systematic increase in T_g with increasing IPC concentration is in agreement with previously reported values where pure BPA−PPDC copolymers exhibit a bulk T_g of only 115 °C, while pure BPA−IPC copolymers exhibit a bulk T_g of 183 °C.[37] As illustrated in Figure 4, T_g and modulus for the aryl−phosphonate copolymers are thickness dependent for the copolymers with 100% and 50% PPDC content but modulus becomes thickness independent when the content of PPDC decreases to 20%. As shown in Figure 4b, the 100% PPDC polymer exhibits a modulus of 2.91 ± 0.23 GPa from 100 nm down to 40 nm, but the modulus significantly decreases as the film thickness decreases below 40 nm to 0.65 ± 0.17 GPa at 10 nm (∼20% of the value for the thickest films). Similarly, the modulus of the 50:50 PPDC:IPC copolymer exhibits thickness-dependent behavior; however, the modulus only begins to decrease from a near constant 2.32 ± 0.15 GPa when the film thickness is less than ≈25 nm. When the film is 10 nm thick, the modulus is reduced to 1.55 ± 0.23 GPa, a 33% decrease from the thickest films. It is interesting to note that T_g of the 50:50 PPDC:IPC copolymer also decreases in this thickness regime, but only a modest decrease in T_g is observed. Increasing the IPC content in the 20:80 PPDC:IPC copolymer leads to a further decrease in the thick film modulus to 1.56 ± 0.21 GPa; however, the modulus becomes thickness independent. This statistically invariant modulus is attributed to an increased stiffness of the copolymer backbone with increasing IPC content. The thin film mechanical behavior of tyrosine-derived polycarbonates, which are similarly stiff, has been reported to be thickness independent for films ranging from 30 to 200 nm; unfortunately, the behavior of thinner films was not reported, but these results agree well with the data presented here.[56] These data illustrate that the thermal and mechanical properties of polymer thin films as determined by ellipsometry and surface wrinkling is strongly dependent upon the flexibility of the polymer chains; the deviations from bulk behavior are significantly reduced or eliminated for polymers containing stiff backbones. One caveat with this prior statement is that some rigid backbone polymers actually have shorter persistence lengths than PS due to the steric hindrances associated with the pendant phenyl groups in PS; PC is a common example. Both sterics and chemical structure of the backbone are likely critical to controlling the physical properties of confinement polymer glasses. There is some evidence in the literature that this is true as McKenna, Soles, and Torkelson have all reported large T_g decreases for PC (even in comparison to PS).[31,33,34] Careful consideration of what defines a rigid polymer is needed to avoid confusion in future discussions on thin film glasses. Interestingly, a similar behavior is obtained when a flexible polymer contains ≈5 % by mass good solvent when examining the T_g[28] and modulus[30] of polymer thin films. These similarities might not be completely unexpected as polymer chains are stretched in the presence of a good solvent, and thus the chain conformation is impacted by the residual solvent. However, this does not agree with the hypothesis that residual solvent might be responsible for the reported decrease in T_g of thin films of PS that can be eliminated by proper annealing.[57] Similarly, Thomas et al. have reported the viscoelastic properties of PS thin films to be dependent upon the casting solvent and bulklike behavior can be recovered through annealing.[58] These experiments suggest that the highly nonequilibrium chain conformation in the vitrified film can lead to significant changes in the polymer properties. In this context, the current results might be explained based upon the chain conformations available that do not allow the film to adopt highly nonequilibrium states, and thus no changes in the physical properties are observed. The solution dynamics of similar polymers with bridged norbornene rings but containing alkyl moieties have shown highly retarded chain relaxations in comparison to standard flexible polymers in solution such as polyisoprene.[59] Additional studies involving Add CENb to examine other thin film properties could be instrumental in understanding the origins for the thickness-dependent properties of many polymer thin films. Additional theoretical and/or simulation work on the impact of chain stiffness on chain conformations and the glass transition near surfaces is also necessary to understand the molecular mechanisms.

■ CONCLUSION

In summary, the modulus and T_g of thin films for a series of poly(aryl phosphonate)s and poly [5-(2-phenylethylnorbornene)] derivatives were determined using wrinkling on an elastic substrate and ellipsometry, respectively. Unlike previous wrinkling studies involving flexible-chain polymers,[53,54] not all polymers examined exhibit a decrease in modulus for their thin films. This behavior appears to be dependent upon the polymer flexibility. The polymers with stiff backbones show no change in modulus as the film thickness is decreased to less than 10 nm; additionally, T_g is independent or only weakly dependent upon film thickness for these polymers.

ASSOCIATED CONTENT

Supporting Information. Thermal expansion curves and thickness dependencies on CTE. This material is available free of charge via the Internet at http://pubs.acs.org.

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