**Poly(methyl methacrylate) Nanotubes in AAO Templates:
Designing Nanotube Thickness and Characterizing the T_g -Confinement Effect by DSC**

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Abstract. We used differential scanning calorimetry (DSC) to study the effect of confinement on the glass transition temperature (T_g) of poly(methyl methacrylate) (PMMA) nanotubes supported in anodic aluminum oxide (AAO) templates. We created nanotubes by wetting templates with polymer melts and developed a design equation relating tube thickness (t_{tube}) with bulk radius of gyration (R_g): ($t_{\text{tube}} \approx 2 R_g + 9 \text{ nm}$). The results indicate that t_{tube} depends on overall conformation and size of the polymer coils and can be tuned at the nanoscale by polymer molecular weight. The T_g of AAO template-supported PMMA nanotubes increases with decreasing t_{tube} , with $T_{g,\text{tube}} - T_{g,\text{bulk}} = 12 \text{ K}$ in 18-nm-thick nanotubes; we attribute the T_g increase to hydrogen bonds between PMMA ester side groups and hydroxyl groups on the surface of the $\gamma\text{-Al}_2\text{O}_3$ templates. Using ellipsometry, we characterized T_g -confinement effects for PMMA films supported on Si/SiO_x, sputtered Al₂O₃ and sapphire ($\alpha\text{-Al}_2\text{O}_3$). Films supported on substrates with higher concentrations of surface hydroxyl groups ($\alpha\text{-Al}_2\text{O}_3 > \text{sputtered-Al}_2\text{O}_3 > \text{Si/SiO}_x$) exhibit larger T_g -confinement effects. The DSC-determined T_g enhancements for nanotubes supported in $\gamma\text{-Al}_2\text{O}_3$ templates fall between the ellipsometry-determined T_g enhancements determined for PMMA films on $\alpha\text{-Al}_2\text{O}_3$ and those for films on sputtered-Al₂O₃. These results show that molecular weight provides for tunability of polymer nanotube thickness in AAO templates, that there is excellent agreement in confinement effects measured by DSC and by ellipsometry, and that T_g can be tuned by modulating the levels of interfacial, polymer-substrate interactions by using surfaces with different chemical or crystallographic properties.

KEYWORDS: AAO template synthesis, polymer nanotubes, T_g -confinement effect

Introduction

Differential scanning calorimetry (DSC) is the most widely accepted and commonly used technique for measuring the glass transition temperature (T_g).¹ However, direct measurements of T_g in ultrathin films by conventional DSC are very difficult because of issues associated with sample preparation and integrity during measurement. Although a typical conventional DSC sample requires only a few milligrams of material for analysis, it is challenging to create ultrathin film samples for DSC because they possess exceedingly little mass, have a tendency to repel each other due to the accumulation of static charge, and require a large amount of time and effort to prepare.²⁻⁶ For example, Fukao and coworkers studied the T_g -confinement behavior of free-standing PS films using DSC.² For the thinnest sample, over 400 thin films were created by spin coating, removing the films from substrates by floating them on water, and then stacking the films into a DSC sample pan. Wang and Zhou studied the T_g of thin films of fully cured epoxy polymer as a function of thickness.⁴ They used a microtome to slice a block of epoxy into films of desired thickness. These were then floated onto water and collected into a DSC sample pan. Several days were required to obtain a sample mass of one milligram.

The difficulty of preparing ultrathin film DSC samples also limits the type of study that can be carried out. Studies conducted by conventional DSC on ultrathin films have aimed at investigating the behavior of free-standing films.²⁻⁶ (It is possible that layered films can weld or heal together during the thermal treatment required for DSC measurements of T_g , meaning that the DSC-measured T_g 's can reflect some combination of free-standing film behavior and effects of welding together of layers, which modifies effective film thickness). However, it is also of scientific interest to understand how the presence or absence of interactions between a polymer and a substrate affect the T_g -confinement behavior.⁷⁻³³ For example, it is well established that for supported films of linear polymer chains, T_g decreases as a function of decreasing thickness in cases where there is little or no interaction between polymer and substrate, e.g., polystyrene (PS) films supported on Si/SiO_x.^{7,10-12,16,17,34} In contrast, an increase in T_g with confinement is observed in systems with sufficiently large attractive polymer-substrate interactions, e.g.,

poly(methyl methacrylate) (PMMA) films supported on Si/SiO_x.^{8,13,19} Any attempt to draw comparisons between the effects of different substrates on DSC-determined T_g -confinement behavior in supported, ultrathin polymer films would be exceedingly complex. Furthermore, such films would be subject to uncertainty regarding welding/healing of layers during DSC measurement.

Development of flash DSCs has made it easier for film analysis because a single film is sufficient for measurement using this technique. However, typically a layer of grease or oil is used to suspend the film on top of the sensor in order to improve thermal conductivity and sensitivity.³⁵ This grease or oil has the potential to plasticize, destabilize and/or interact with the polymer. It is possible to deposit films directly onto the back of the calorimetric sensor, but this limits the range of polymer-substrate interactions which can be investigated.^{35,36}

Direct conventional DSC measurement of thin films is challenging due to issues regarding sample preparation and the types of experiments which can be done. However, a number of studies have successfully utilized DSC to study the T_g -confinement behavior of polymers confined to other geometries. Understanding the behavior of polymers in other geometries gives insight into the factors which affect T_g and opens up the opportunity to better control or tune properties. Recent DSC studies on the T_g -confinement behavior of aqueous dispersions of polymer nanospheres and quasi-nanospheres by Priestley and coworkers^{37–39} and Feng et al.^{40,41} have reported that T_g decreases with decreasing sphere size.

Polymer nanorods and nanotubes are also of interest because of their potential technological applications and the opportunity to better understand how curvature affects T_g -confinement effects. Template synthesis can be employed to create large arrays of polymer nanorods or nanotubes.^{42–70} Three studies have employed DSC to investigate the T_g -confinement behavior of polymer nanorods supported in anodic aluminum oxide (AAO) templates.^{67,68,71} Li et al.⁶⁷ reported that AAO-template-supported PMMA nanorods exhibited two T_g 's, one higher and one lower than the bulk T_g of the polymer. This was explained in terms of a two-layer model: polymer near the polymer-template interface possessed a higher T_g due to attractive interactions

with the substrate, and polymer near the core of the nanorods possessed a lower T_g due to poorer packing of the polymer chains. Reid et al.⁶⁸ studied the T_g behavior of polycarbonate nanorods in AAO and found that surface modifications of the template changed the magnitude of the confinement effect and the thermal stability of the polymer. Only one DSC study has been reported on the vitrification behavior of polymer nanotubes with confinement, which focused on PS nanotubes made by solution wetting of AAO templates.⁷²

Creating nanotubes with uniform morphologies and controlling their wall thickness has been a major issue hindering their study.^{53,55,56,69,73} The simplest approaches for creating nanotubes are to infiltrate a polymer solution or melt into AAO templates with cylindrical pores.^{42–66,69,70} Polymer is deposited onto the surface of the template walls, resulting in negative replication of the size, shape and length of the pore morphology.^{42,49} With solution infiltration, the wall thickness is a function of solvent species, polymer molecular weight (MW) and concentration, and template size.^{42,45,47–51,53,54,57,70} However, the uniformity and reproducibility of nanostructures produced by this method can be unpredictable. Holes or undulations often form due to solvent evaporation or the evolution of Rayleigh instabilities during annealing.^{53,55,56,69,73} Extensive drying must be carried out because residual solvent can alter tube morphology and affect the polymer bulk T_g and T_g -confinement effects.^{24,74} Melt infiltration is advantageous because it is solventless, yielding more uniform and reproducible nanostructures.⁴⁶ However, the ability to rationally tune tube thickness has never been demonstrated using this technique.

Here, we demonstrate that the wall thickness of polymer nanotubes can be tuned in a straightforward manner by changing the MW of the polymer infiltrated during melt infiltration. Our results indicate that tube thickness is directly related to the conformation and size of the polymer coils, which can be quantified using the radius of gyration (R_g) of bulk polymer. This leads to a simple design equation which can be used in experimentally controlling the wall thickness of the nanotubes. Concurrent with developing this new approach, we investigated and compared the T_g -confinement behavior of template-supported PMMA nanotubes and substrate-supported PMMA thin films using DSC and ellipsometry, respectively. Our results show that

MW provides for tunability of polymer nanotube thickness in AAO templates, that there is excellent agreement in confinement effects measured by DSC for nanotubes and by ellipsometry for thin films, and that T_g can be tuned by modulating the levels of interfacial, polymer-substrate interactions by using surfaces with different chemical or crystallographic properties.

Experimental

Materials and Sample Preparation

Nearly monodisperse, anionically polymerized PMMA samples with nominal molecular weight (MW) of 26 kg/mol, 61 kg/mol, 188 kg/mol, 480 kg/mol and 714 kg/mol were obtained from Pressure Chemical. Disperse PMMA samples were obtained from Scientific Polymer Products (cat# 037C-lot#9 and cat# 037Sc). The disperse samples were washed and precipitated three times using toluene as solvent and methanol as precipitant in order to remove commercial additives that could affect the bulk T_g and confinement effects.^{24,74,75} The average MW's of these washed and precipitated samples were determined using universal calibration curves from gel permeation chromatography ($M_n = 65$ kg/mol and $M_w = 97$ kg/mol; $M_n = 224$ kg/mol and $M_w = 380$ kg/mol). A third disperse sample was created by solution blending disperse $M_w = 380$ kg/mol polymer with monodisperse MW = 26 kg/mol polymer in a 0.8:0.2 weight ratio, yielding a sample with $M_n = 100$ kg/mol and $M_w = 310$ kg/mol. The tacticity of all polymers was determined using C-13 NMR and found to be ~3% isotactic, ~57% syndiotactic, ~40% heterotactic (see supplementary information). Nearly monodisperse, anionically polymerized PS with a nominal MW of 90 kg/mol was obtained from Scientific Polymer Products.

Synthesis and Characterization of Template-Supported PMMA Nanotubes

AAO templates (Anopore inorganic membranes) with a pore diameter of ~330 nm as determined from scanning electron micrographs (nominal size of 200 nm as reported by supplier) were obtained from Whatman International. Templates were degreased using acetone and then cleaned under a 200 W argon/oxygen plasma using a South Bay plasma cleaner for 10 min. Polymer solutions (10 wt%) were created by dissolving polymers in toluene. Films were created

by solution casting onto degreased Kapton sheets and annealing at 433 K for 2 hr in air. The films were peeled from the Kapton after cooling. Synthesis of template-supported nanotubes was carried out by placing a film on top of a bare template and melt infiltrating at 523 K for 15 min under flowing Ar (Figure 1). The samples were then cooled to room temperature at 40 K/min. Residual polymer was removed by polishing the template surface with a SiC 600-grit paper.

Figure 1: Preparation of template-supported PMMA nanotubes using a melt infiltration technique. Polymer films were placed onto bare AAO templates and then infiltrated at 523 K for 15 min under flowing Ar. At high temperatures and under complete wetting conditions,^{76,77} the polymer melt spontaneously wets the template in order to stabilize the template-air interface. After infiltration, the surface was polished using SiC grit paper to remove remaining polymer at the surface.

The T_g of template-supported PMMA nanotubes was measured using a Mettler Toledo 822e differential scanning calorimeter. A DSC sample was created by taking a piece of infiltrated and surface-polished template and placing it into a 40 μ l Al DSC pan. Samples were annealed at 433 K for 10 min and cooled to 313 K at a rate of 40 K/min. T_g measurements (onset method) were taken on second heat from 313 to 433 K at a rate of 10 K/min. (By definition, T_g is measured on cooling; however, typically T_g measurements using DSC are taken on heating.) In the absence of physical aging effects, the value of T_g determined on heating is very similar to the value of T_g determined on cooling; a previous study found that the values of T_g obtained via DSC on heating and cooling differed by only 0.5–1.4 K.⁷⁸ For this study, we employ DSC to measure T_g on heating. We note that 0.5–1.4 K differences in T_g due to the direction of measurement are small relative to the magnitude of T_g -confinement effects.

For the four PMMA samples with M_w of 61 kg/mol, 97 kg/mol, 188 kg/mol and 380 kg/mol, a portion of the infiltrated nanotubes was dissolved in THF (10 mg polymer with 10 mL solvent) and analyzed using gel permeation chromatography (GPC) to test for any degradation in MW after thermal treatment (see supplementary information). At most, only 2-4% decreases in MW averages were observed after exposing the polymer to infiltration conditions, so changes to the T_g from bulk response cannot be attributed to changes in MW.

Morphological and size analysis of the nanotubes was conducted using scanning electron microscopy (SEM). Nanotubes were released from the template by taking a piece of infiltrated template and immersing it in a 1 M NaOH solution for 20 min. The tubes were collected and rinsed in distilled water before being mounted onto carbon tape. A thin layer of osmium was sputtered onto the surface to prevent charging. This procedure was carried out for all template-supported PMMA nanotube samples. A Hitachi SU 4800 SEM was used to create electron micrographs of the nanotube samples. Tube thickness was analyzed by measuring the distance between the inner and outer rim of a nanotube using ImageJ. This process was carried out for 50-100 nanotubes to determine the size distribution for each sample. Finally, the length of the nanotubes was determined by measuring the overall tube length at several different locations within each sample.

Fabrication and Characterization of Silica- and Alumina-Supported PMMA and PS Thin Films

Silicon (WaferNet Si <100>) and sapphire (Aldrich C-axis EPI polished Hemcor) wafers were degreased in toluene and then plasma cleaned under a 200 W argon/oxygen plasma using a South Bay PC 2000 plasma cleaner for 10 min. A set of silicon wafers was coated with alumina using an AJA International High Vacuum D.C. magnetron sputter coater. Sputtering was conducted at room temperature with an aluminum target for 1 hr using a power of 100 W and a flow rate of 20 SCCM for Ar and 4 SCCM for O₂. The thickness of the alumina layer was measured using an M-2000D spectroscopic ellipsometer (J.A. Woollam Co., Inc). Delta and psi were measured at wavelengths from 400 to 1000 nm with an incident angle of 65°. A layer model consisting of a silicon substrate with a 2-nm-thick native SiO₂ layer and a top layer of

alumina was created. The refractive constants of the silicon and silica layers were taken from literature data.^{79,80} A Cauchy dispersion model was employed to fit the delta and psi values in order to determine the thickness of the alumina layer.⁸¹ At room temperature, the alumina layer was found to be 12 nm thick.

Dilute polymer solutions (0.2 to 2.0 wt%) of PMMA ($M_w = 97$ kg/mol, 380 kg/mol and 714 kg/mol) and PS (nominal MW = 90 kg/mol) were created by dissolution in toluene (Sigma Aldrich). Polymer thin films were created by spin coating onto the wafers and annealing in air at 433 K for 2 hr. Delta and psi were measured at wavelengths from 400 to 1000 nm with an incident angle of 65°. The thickness and index of refraction of the supported thin films were obtained by employing layer models to fit delta and psi.⁸¹ For sapphire-supported thin films, the layer model consisted of a single alumina layer and a polymer layer on top. For films supported on sputtered alumina, the layer model consisted of a silicon substrate with a 2-nm-thick native SiO₂ layer, a layer of alumina 12 nm thick and a layer of polymer on top. For films supported on silicon wafers, the layer model consisted of a silicon substrate with a 2-nm-thick native SiO₂ layer and a layer of polymer on top. The refractive index of the alumina, silica and silicon layers were taken from literature.^{79,80} A Cauchy dispersion model was employed in order to determine the index of refraction and thickness of the polymer layer.⁸¹ The accuracy of the models was verified by placing films of identical thickness on top of each substrate and comparing the thicknesses obtained from the Cauchy fits.

Ellipsometric determinations of T_g for supported PMMA thin films were carried out by heating to 463 K, holding for 20 min and then cooling to 313 K at a rate of 1 K/min. Measurements for supported PS thin films were carried out in a similar manner but were only heated to/cooled from 403 K. The index of refraction was obtained from ellipsometric measurements. The indices of refraction in the rubbery and glassy regimes were fit using linear regression, and T_g was determined from the intersection of the lines.^{25,82}

Results and Discussion

Design and Fabrication of Supported PMMA Nanotubes

Melt infiltration of eight different PMMA samples into AAO templates was carried out at 523 K for 15 min under flowing Ar. Except for the 480 kg/mol and 714 kg/mol samples, infiltration was successful in yielding large arrays of polymer nanotubes (Figure 2). The nanotubes possessed diameters (~ 330 nm) and lengths (~ 60 μ m) similar to that of the template, indicating that the template walls were completely wetted by the polymer during infiltration. In contrast, infiltration of the 480 kg/mol and 714 kg/mol samples yielded nanorods with a diameter of ~ 330 nm and length of ~ 300 nm, which indicates that only partial wetting of the template occurred.

Figure 2: Scanning electron micrographs: a) End view of the nanotubes formed from melt infiltration of 26 kg/mol PMMA into AAO. The nanotubes were removed from the template in order to conduct SEM analysis. The size distribution was determined by measuring tube wall thicknesses using ImageJ and calculating the number and mass %. The number and mass average thicknesses were 16 and 17 nm, respectively. b) Side view of the nanotubes, which indicates that the tubes possessed an overall length of ~ 60 μ m (the same thickness as the template) and demonstrates that complete wetting of the templates occurred during infiltration.

These results are consistent with previous work in which the wetting transition temperature (T_{wet}) of polymers in AAO templates has been observed to increase with polymer MW.⁴⁹ Above T_{wet} , nanotubes are formed when polymers rapidly and spontaneously wet the surface of the template in order to lower the total system energy. Comparatively, below T_{wet} , polymers only partially wet the template surface. In this case, formation of nanorods occurs via capillary action. While capillary action is also present in the supported nanotubes, the timescale

of the filling process is several orders of magnitude longer than that of tube formation, so the structure of the nanotubes does not change for short annealing times at temperatures slightly above T_g .⁴⁹

The nanotube wall thickness (t_{tube}) was determined from electron micrographs (Figure 2) by measuring 50-100 nanotubes using ImageJ processing software (Table 1) and calculating the mass-average wall thickness, which we take as t_{tube} . This calculation was done by weighting the thickness of each tube according to its cross-sectional area and then determining the weighted average. A mass-average thickness was used because T_g was measured using DSC. Other things being equal, the calorimetric measurable scales with mass, i.e., a thicker nanotube contributes more to the DSC signal in proportion to its mass. The mass- and number-average thicknesses for a nanotube sample were very similar, differing by 0 to 4 nm.

Table 1: Number and mass average thickness of PMMA nanotubes formed after infiltrating polymers with different MWs and dispersity. R_g was determined using experimentally determined scaling parameters relating R_g and the MW; for monodisperse polymer, $R_g = 0.025 \cdot \text{MW}^{1/2} \text{ nm}^{83}$ and for disperse polymer $R_g = 0.025 \cdot M_w^{1/2} \text{ nm}$ where M_w is the weight average MW.

PMMA		Mass. avg. thickness (nm) [^]	Number avg. thickness (nm) [^]	R_g (nm)
M_w (kg/mol)	$\mathcal{D}$			
26	1.11	17	16	4.0
61	1.08	22	22	6.2
97 [*]	1.5	25	24	7.8
188	1.09	31	29	11
310 ^{**}	3.0	40	37	15
380 [*]	1.7	39	35	15
480 ^{>}	1.09	N/A	N/A	17
714 ^{>}	1.09	N/A	N/A	21

* Commercial samples washed to remove low MW additives which can affect polymer bulk T_g and T_g -confinement behavior. GPC analysis conducted to determine M_w after cleaning procedure.

** Mixture of disperse 380 kg/mol PS and monodisperse 26 kg/mol PS samples with an approximate weight ratio of 4 to 1.

> Temperature was insufficiently high to promote complete wetting of the template. Capillary filling of the templates occurred instead and resulted in the formation of nanorods.

[^] The uncertainty of the thickness measurement was ± 1 nm except for the 380 kg/mol PMMA where it was ± 2 nm.

Analysis of the results shows that t_{tube} increases as a function of the square root of the weight average molecular weight ($M_w^{1/2}$) for both monodisperse and disperse polymer samples (Figure 3a). The results were also analyzed by plotting t_{tube} as a function of the square root of the number average molecular weight ($M_n^{1/2}$); however, the fit for the disperse samples was poor, indicating that longer chains have a greater influence on t_{tube} than shorter chains (Figure 3b).

Figure 3. Relationship between t_{tube} of template-supported PMMA nanotubes and a) $M_w^{1/2}$ and b) $M_n^{1/2}$. The dotted line is a best fit to the data. The poor fit for the disperse samples in b) indicates that longer chains exhibit a greater influence on determining nanotube thickness than shorter chains.

It is important to note that the thickness- $M_w^{1/2}$ relationship has been previously observed in polymer films formed from adsorption of dilute solutions and spreading of melts^{26,84-106} on flat substrates and in other geometries under similar conditions.^{84,107,018} This scaling behavior originates from the conformation of polymer chains and has been explained in terms of the degree of polymerization N .^{91,92,108-111} Because MW is directly proportional to N , t_{tube} also scales with $N^{1/2}$. Bruinsma's layer model,¹¹² which describes the overall chain conformation and wetting behavior of polymers on flat substrates, is useful in understanding the linear relationship between t_{tube} and $N^{1/2}$. We apply this model while noting that during melt infiltration the walls of the template are wetted vertically and in a circumferential manner to yield tubes. In this case, the nanotube radius of curvature (~ 165 nm) is large compared to t_{tube} so the profile can be roughly approximated as a film supported on a flat substrate. Based on this model, the nanotube consists

of a layer of polymer chains adsorbed to the polymer-substrate interface and another layer of unattached polymer chains partially enmeshed within the adsorbed layer.

The adsorbed polymer chains exhibit random walk statistics,^{109,113-115} resulting in a thickness which scales with $N^{1/2}$ similar to polymer chains in the bulk. The chains adopt a trains (adsorbed segments), loops (free segments connecting trains) and tails (unattached chain ends) conformation which is independent of the chemical structures of the polymer and substrate.¹¹⁶⁻¹²⁰ The remaining unattached chains in the enmeshed layer also exhibit random walk behavior with a size that increases with $N^{1/2}$. This is because infiltration occurs spontaneously in the rubbery state where non-equilibrium stresses are not expected to significantly distort the shape of the coil.¹²¹⁻¹²³ The combined thickness obtained from the adsorbed and enmeshed polymer layers is then a function of $N^{1/2}$ or $M^{1/2}$, where M is the MW of polymer with degree of polymerization N .

The relationship between t_{tube} and overall polymer conformation was utilized to develop a design equation. Values of R_g , listed in Table 1, were determined from experimentally derived scaling parameters relating R_g with the MW of the polymer,⁸³ resulting in eqn. (1):

$$R_g = 0.025 M^{1/2} \quad (1)$$

where R_g and M have units of nm and g/mol, respectively. In eqn. (1), M represents the MW for monodisperse polymers and M_w for disperse polymers. Figure 4 illustrates the linear relationship between t_{tube} and R_g . A fit to the data for both monodisperse and disperse PMMA samples (solid line in Fig. 2) results in eqn (2):

$$t_{\text{tube}} \approx 2 R_g + 9 \text{ nm} \quad (\text{for } 4.0 \text{ nm} \leq R_g \leq 15 \text{ nm}) \quad (2)$$

Figure 4 also shows the results from a study by Silberzan and Léger⁷⁷ regarding the thicknesses of polydimethylsiloxane (PDMS) films formed from spreading droplets on flat surfaces. A similar linear relationship (film thickness = $2 R_g + 3 \text{ nm}$) is determined based upon their data. The generality of the linear relationships between R_g and t_{tube} for nanotubes and R_g and thickness for thin films indicates that the thickness of films or tubes formed from melt wetting of high energy surfaces can be predicted and tuned if the R_g of bulk polymer is known.

Additionally, these results indicate that the spreading behavior and average polymer chain

conformations on flat surfaces are similar to those on the curved AAO templates. This similarity is reasonable considering the large radius of curvature of the templates used here (~ 165 nm).

Figure 4. Relationship between R_g and t_{tube} for template-supported PMMA nanotubes. The thicknesses of films formed from spreading PDMS melts on silica from Silberzan and Léger are also plotted against R_g .⁷⁶ The solid and dotted lines represent a best fit to the data for the template-supported PMMA tubes ($t_{\text{tube}} \approx 2 R_g + 9$ nm) and the supported PDMS thin films (thickness $\approx 2 R_g + 3$ nm).

T_g -Confinement Behavior of Supported PMMA Nanotubes and Films

Shown in Fig. 5 are the DSC heat flow curves for bulk polymer and template-supported nanotubes consisting of monodisperse PMMA with MW = 61 kg/mol. The supported nanotubes had a $t_{\text{tube}} = 22$ nm and exhibited a substantial enhancement in T_g over bulk PMMA, with $T_{g,\text{tubes}} - T_{g,\text{bulk}} = 9$ K. The increase in T_g with confinement is due to the attractive hydrogen-bonding interactions between the PMMA ester groups and the hydroxyl groups^{8,27,40} on the template surface. These attractive interactions between the polymer and template surface result in decreased segmental mobility near the interface which can propagate into the nanotube interior.^{20,28}

These T_g -confinement effects can only be clearly observed if the surface of the infiltrated templates are polished in order to remove residual polymer remaining on the upper surface of the template after melt infiltration. If this layer is not removed, two T_g 's are observed: a bulk-like T_g corresponding to residual polymer film at the upper surface of the template and a T_g corresponding to the supported nanotubes. (See supplementary information for a comparison

between melt infiltrated samples with and without surface polishing.) The T_g measurements shown in Figure 5 and in the remaining text are for samples where the surface layer was removed using the polishing step in order to isolate the behavior of the supported PMMA nanotubes.

Figure 5. DSC-determined heat flow curves for bulk PMMA powder and AAO template-supported PMMA nanotubes for the same MW polymer (61 kg/mol). T_g was defined as the onset of the transition and is illustrated by the arrows. A T_g increase of 9 K was observed for template-supported nanotubes of $t_{\text{tube}} = 22$ nm compared to bulk T_g .

The size dependence of the T_g -confinement effect was investigated by comparing DSC heat flow curves of template-supported nanotubes as a function of t_{tube} . Results are shown in Fig. 6, where the abscissa is given by normalized absolute temperature, $T/T_{g,\text{bulk}}$, in order to account for small differences in bulk T_g of the different PMMA samples in the nanotubes of different thickness. (See Table 1 for values of $T_{g,\text{bulk}}$ and $T_{g,\text{tubes}} - T_{g,\text{bulk}}$.) In this study, different polymer MW's were used to vary t_{tube} . Comparisons between different MW PMMA samples (of similar tacticity) can be carried out because T_g -confinement effects of supported PMMA samples are independent of MW except at very low MW.²⁷ Enhancements in T_g were observed as the thickness of the supported nanotubes was decreased. The length scales over which T_g -confinement effects are observed are consistent with previous research showing that perturbations caused by an interface can propagate (in a decreasing manner) a few tens of nanometers into the film interior.^{20,28,124,125}

Figure 6. DSC heat flow vs. $T/T_{g,bulk}$ for AAO template-supported nanotubes. The abscissa is given by normalized absolute temperature, $T/T_{g,bulk}$, in order to account for small differences in bulk T_g of the different PMMA samples in the different nanotube samples. Arrows indicate the location of the T_g , defined as the onset of the transition. The thinner nanotubes exhibited larger T_g increases than the thicker nanotubes and illustrate the size-dependence of the T_g -confinement effect.

We compared the T_g -confinement behavior exhibited by PMMA template-supported nanotubes with the behavior of supported thin films of PMMA. Films were created by spin coating PMMA solutions onto Si/SiO_x, sapphire (α -Al₂O₃), and sputtered alumina (sput-Al₂O₃) substrates and characterized via ellipsometry. The temperature dependence of the index of refraction in the rubbery and glassy regimes was fit using linear regression analysis, and the intersection of the lines was used to determine T_g ^{25,82} (see supplementary information). Figure 7a shows the T_g -confinement behavior of the supported PMMA films. In agreement with previously reported studies,^{8,13,15,19,20} a small increase in $T_{g,film} - T_{g,bulk}$ above 0 K was observed for PMMA films supported on Si/SiO_x with decreasing thicknesses below ~30 to 40 nm. Interestingly, PMMA films supported on α -Al₂O₃ exhibited T_g increases with confinement that were a factor of 5 to 7 greater than those observed for Si/SiO_x-supported thin films of similar thickness. PMMA films supported on sputtered Al₂O₃ exhibited confinement effects intermediate to those of films supported on α -Al₂O₃ and those supported on Si/SiO_x.

Table 2: T_g of template-supported nanotubes and bulk polymer samples used in this study. Multiple tube samples were created for some of the polymers. Variations in t_{tube} occur due to differences in the template morphology and surface roughness from template to template.^{126,127}

PMMA		t_{tube} (nm) [^]	$T_{g,\text{bulk}}$ (K) ^{^^}	$T_g - T_{g,\text{bulk}}$ (K) ± 1 K
M_w (kg/mol)	$\bar{M}_n$			
26	1.11	17	373	12
61	1.08	22	386	9
		21		7
97 [*]	1.5	24	379	6
		25		5
188	1.09	30	387	5
		31		3
310 ^{**}	3.0	40	391	0
380 [*]	1.7	36	391	0
		41		0
480 ^{>}	1.09	N/A	391	N/A
714 ^{>}	1.09	N/A	395	N/A

^{*} Commercial samples were washed to remove low MW additives which can affect polymer bulk T_g and T_g -confinement behavior. GPC analysis conducted to determine M_w after cleaning procedure.

^{**} Mixture of disperse 380 kg/mol PS and monodisperse 26 kg/mol PS samples with an approximate weight ratio of 4 to 1.

[>] Temperature was insufficiently high to promote complete wetting of the template. Capillary filling of the templates occurred instead and resulted in the formation of nanorods.

[^] The uncertainty of t_{tube} was ± 1 nm for each set of tubes measured from a particular template.

^{^^} The uncertainty of T_g measurements is ± 0.5 K. Values are rounded to the nearest whole number.

Figure 7b compares the T_g -confinement behavior of the AAO template-supported PMMA nanotubes with the best fit curves of the T_g -confinement behavior of supported thin films. The AAO templates used in this study consisted of γ -Al₂O₃.¹²⁸ Overall, the magnitude of T_g -confinement effects for the supported thin films and nanotubes decreased in the following order: α -Al₂O₃ films > γ -Al₂O₃ tubes > sput-Al₂O₃ films > Si/SiO_x films.

As a control study, the T_g -confinement behavior of PS films supported on Si/SiO_x, sput-Al₂O₃ and α -Al₂O₃ were also measured by ellipsometry; results are given in Figure 7c. Within experimental error, identical T_g -confinement behavior was observed regardless of the substrate type. This invariant response as a function of substrate is expected because there are no attractive polymer-substrate interactions between PS and these substrates beyond weak van der Waals

interactions.^{76,129-131} The T_g -confinement behavior of such supported PS films is thus attributable only to free-surface effects and any intrinsic effects of confinement not associated with surfaces or interfaces.^{7,10-12,28-30,124}

Figure 7. a) Ellipsometric determinations of PMMA films supported on a variety of substrate types. Significant increases in T_g as large as 16 K were observed for films supported on α - Al_2O_3 compared to the bulk T_g . The magnitude of T_g -confinement effects for the supported thin films decreased in the following order: α - Al_2O_3 films > γ - Al_2O_3 tubes > sput- Al_2O_3 films > Si/SiO_x films. The curves on the figure correspond to best fits of the data. b) Comparison between the T_g -confinement behavior of template-supported PMMA nanotubes and supported PMMA thin films. The DSC-determined T_g enhancements for nanotubes supported in γ - Al_2O_3 templates fall between the ellipsometry-determined T_g enhancements determined for PMMA films on α - Al_2O_3 and those for films on sputtered- Al_2O_3 . c) T_g -confinement behavior of PS thin films supported on α - Al_2O_3 and sputtered- Al_2O_3 . The solid curve denotes the best fit of T_g -confinement data for silica-supported PS thin films from Keddie and coworkers.⁸

Results from previous studies suggest that the magnitude of T_g -confinement effects attributable to attractive interfacial interactions depends on the interfacial concentration and

strength of such interactions between the polymer and the substrate.^{17,19,20,31,132-135} For polymers which undergo hydrogen bonding with hydroxyl groups on the substrate surface, the magnitude of T_g -confinement effects depends on the electronegativity of the bonding atom. For example, poly-2-vinylpyridine (P2VP) (atactic) thin films exhibit much larger T_g increases than (atactic) PMMA films of similar thickness.^{19,29,29,136} This can be attributed to the greater hydrogen bond strength in P2VP (O-H--N: 29 kJ/mol) compared to that of PMMA (O-H--O: 21 kJ/mol).¹³⁷ The surface chemistry can be expected to affect the bond strength in a similar manner. In some cases, polymer tacticity can also affect the magnitude of T_g -confinement effects, as shown in a study of films of PMMA of various tacticity supported on Si/SiO_x substrates.¹³

The PMMA samples in this study possessed nearly identical tacticities. Thus, any variation in T_g -confinement behavior is attributed to the differences in the concentration of hydrogen bonding sites (surface hydroxyl groups) on the various substrate surfaces. Crystallographic data indicate that the monolayer capacities of surface hydroxyl groups for α -Al₂O₃¹³⁸, γ -Al₂O₃¹³⁹ and quartz-SiO₂¹³⁸ surfaces are 19, 13 and 8 OH/nm², respectively. The sputtered-Al₂O₃ sample was fabricated at room temperature in order to obtain amorphous Al₂O₃.^{140,141} Amorphous surfaces are expected to have fewer hydroxyl groups than the surfaces of their crystalline forms because the disordered orientation of metal-oxygen M-O atoms restricts the extent and stability of the hydroxyl groups.¹⁴² The Si/SiO_x substrate possessed an amorphous surface layer of silica because formation of oxide scales on Si yields amorphous silica.^{143,144} Experimentally, full monolayer hydroxyl group capacities are unlikely to be achieved so the actual hydroxyl group concentrations are generally lower: α -Al₂O₃ (~15 OH/nm²),^{145,146} γ -Al₂O₃ (~10 OH/nm²),¹⁴⁶ quartz-SiO₂ (~4 OH/nm²)¹⁴⁷ and amorphous-SiO₂ (~2 OH/nm²).¹⁴⁸ Based on this information, the concentration of surface hydroxyl groups decreases as follows: α -Al₂O₃ films > γ -Al₂O₃ tubes > sput-Al₂O₃ films > Si/SiO_x films. This is the same order in which the strengths of the T_g -confinement effect decrease.

This study has provided the first demonstration that differences in T_g -confinement behavior associated with attractive polymer-substrate interactions can occur with identical

polymers when supported on substrates of identical composition but different crystal structure. These results strongly reinforce the idea that T_g -confinement behavior is affected by the number and strength of attractive polymer-substrate interactions.^{17,19,20,31-33,132,133,135} These results have a number of implications regarding the T_g -confinement behavior of polymer nanocomposites.^{132,149-151} If different studies of the confinement behavior of a given polymer-nanofiller hybrid do not employ nanofiller of identical size and monolayer capacity of surface hydroxyl groups, then quantitatively different T_g -confinement effects may be expected for polymers that can undergo hydrogen bonding. This is true even in the case of identical dispersion levels of nanofiller in polymer. Additionally, many companies supply nanoparticles which have been coated in order to facilitate their dispersion in water or other solvents or to compatibilize them with polymer blends.^{152,153} Such factors may explain the several studies that report measurements of a decrease in T_g of PMMA upon addition and dispersion of commercial alumina nanoparticles;^{132,149,150} this T_g decrease is not in accord with expectations based on hydrogen bonding at the polymer-nanoparticle interface.

The results in Fig. 7b also indicate that for a given polymer system the T_g -confinement behavior of supported thin films and nanocomposites can be tuned by changing the substrate material, its crystal structure or employing coatings with a particular concentration of interacting groups. For example, the concentration of surface hydroxyl groups has been previously documented for a variety of substrates (i.e., OH/nm²: SiO₂ < Ta₂O₃ < TiO₂ < Cr₂O₃ < Cr₂O₃ < Al₂O₃).¹⁴⁵ By taking advantage of this information in future studies, the T_g -confinement effect (and related confinement effects, e.g., physical aging^{20,29,132,154}) can be modulated using different substrate materials, crystal structures, etc.

The comparison in Fig. 7b between the T_g -confinement behavior of the AAO template-supported nanotubes and the alumina-supported thin films suggests that geometric effects are insignificant for the nanotubes employed in this study. The profile of a supported nanotube can be approximated as a supported thin film because the radius of curvature of the tubes (~165 nm) is very large in comparison to the thicknesses at which the confinement effect is evident.^{20,28}

Alternatively, a characteristic size scale (t^*) can be used to compare the T_g -confinement effects between nanotubes and thin films. Here, we take t^* to be the ratio of volume to surface area over which perturbations to T_g are expected. Because perturbations to T_g are expected at both the free surface and the polymer-substrate interface in PMMA thin films and PMMA nanotubes supported on Al_2O_3 , we define t^* as $h/2$ for thin films where h is the film thickness and $t_{\text{tube}}/2$ for nanotubes.¹⁵⁵ The values of $T_g - T_{g,\text{bulk}}$ of template-supported PMMA nanotubes and thin films are plotted as a function of t^* in Figure 8. These results show that the magnitude of T_g -confinement effects for the supported thin films decreases in the following order: $\alpha\text{-Al}_2\text{O}_3$ films > $\gamma\text{-Al}_2\text{O}_3$ tubes > sput- Al_2O_3 films > Si/SiO_x films, which is consistent with the decrease in the density of hydroxyl groups present on the surface of these substrates. Figure 8 also demonstrates that the confinement geometries employed in this study have little or no effect on the T_g -confinement behavior.”

Figure 8. The T_g -confinement behavior of supported PMMA thin films and template-supported nanotubes as a function of characteristic size t^* . The magnitude of T_g -confinement effects for the supported thin films decreased in the following order: $\alpha\text{-Al}_2\text{O}_3$ films > $\gamma\text{-Al}_2\text{O}_3$ tubes > sput- Al_2O_3 films > Si/SiO_x films, and is consistent with the decrease in the density of hydroxyl groups present on the surface of these substrates.

Conclusions

A method of creating polymer nanotubes with rationally tunable wall thicknesses using melt infiltration into AAO templates was demonstrated for the first time. Nanotubes were created

by wetting AAO templates with monodisperse and disperse PMMA melts. Nanotube wall thickness increased linearly with $M_w^{1/2}$ for both monodisperse and disperse samples. A simple design equation relating PMMA t_{tube} and radius of gyration, R_g , was developed ($t_{\text{tube}} \approx 2 R_g + 9$ nm, with $4.0 \text{ nm} \leq R_g \leq 15 \text{ nm}$). This relationship allows t_{tube} to be changed in a straightforward manner by varying polymer MW.

The T_g -confinement behavior of the PMMA nanotubes supported in γ - Al_2O_3 AAO templates was measured by DSC and compared with the T_g -confinement behavior of PMMA films supported on Si/SiO_x, sputtered- Al_2O_3 and α - Al_2O_3 substrates. The concentration of hydroxyl groups on the substrate surface had a significant effect on the strength of T_g -confinement effects. The magnitude of T_g -confinement effects decreased as follows: α - Al_2O_3 films > γ - Al_2O_3 tubes > sput- Al_2O_3 films > Si/SiO_x films. This was the same order in which the concentration of surface hydroxyl groups on the substrates decreased. These results indicate that T_g -confinement effects for attractive polymer-substrate systems can be tuned by modulating the levels of interfacial, polymer-substrate interactions by using surfaces with different chemical or crystallographic properties. In contrast to the T_g -confinement behavior of the PMMA thin films, supported PS thin films exhibited T_g -confinement effects which were independent of substrate type. The invariance with substrate type for PS thin films can be attributed to the inability of PS to form attractive interactions with hydroxyl groups on the surfaces of Si/SiO_x and Al_2O_3 . Finally, a characteristic size was used to compare the T_g -confinement behavior of the template-supported PMMA nanotubes and supported PMMA films. These results showed excellent agreement between the DSC-determined T_g -confinement effects for PMMA nanotubes supported in AAO templates and the ellipsometrically-determined effects for PMMA films supported on flat alumina substrates. Thus, the geometry associated with confinement had an insignificant effect on the T_g -confinement behavior of the supported nanotubes created in this study.

Supporting Information

Further information regarding the determinations of PMMA sample tacticity, molecular weight change before/after infiltration, DSC T_g behavior of template-supported PMMA nanotubes and ellipsometric determinations of T_g behavior for supported PMMA thin films can be found in the supplementary information. This information can be obtained free of charge at <http://pubs.acs.org>.

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Supported Tubes

Attractive interactions,
chain mobility $\downarrow$, $T_g \uparrow$

Supported Films

Free surface, chain
mobility $\uparrow$, $T_g \downarrow$