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Supplementary Information for

Estimating the Density of Thin Polymeric Films Using Magnetic Levitation

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S1. Experimental Methods

Materials. Ultra-flat (roughness < 0.5 nm) P-type silicon wafers were purchased from Alpha

Nanotech Inc (ANUF0500S2). Polydisperse polystyrene (PS, Mn = 170,000 Da, PDI = 2.04,

441147-1KG, Batch # 04612CJ) was purchased from Sigma Aldrich. Poly(methyl methacrylate)

(PMMA, Mn = 75,000 Da, PDI = 2.8, CAT # 04553, LOT # 552464) was purchased from

Polysciences Inc. Monodisperse PS (M_n=110,000 Da, PDI = 1.03, Lot # ps100313wa) was

purchased from Polymer Standards Service-USA, Inc. Polyvinyl chloride (PVC, Mn = *high*, PDI

= *unknown*, 81392-10G) , polyetherimide (PEI, Mn = *unknown*, PDI = *unknown*, 700193-250G,

LOT # MKBC0294V), and poly(isobutyl methacrylate) (PIBMA, M_w = 70,000 Da, 181544-

250G, Batch # 04926MH) were purchased from Sigma Aldrich Inc. Polyacrylic acid (PAA, *Mn*

~ 5,000) was purchased from Polysciences Inc. in a 50 % by mass aqueous solution, and then

diluted to 15 % by mass aqueous solution by adding deionized water. SU-8 2000.5 photoresist

was purchased from Kayaku Advanced Materials, Inc. (formerly MicroChem Corp.). NOA-61

optical adhesive was purchased from Norland Products.

Preparation of films. For PS, PMMA and PIBMA, a stock solution was prepared in toluene at a

concentration of 100 mg/ml (that is, 10 mg of solid polymer per mL of solvent) by stirring

overnight at a temperature of 50 °C and then passing the solution through a 1 µm PTFE filter.

Solutions with 75 mg/ml, 50 mg/ml, 25 mg/ml, 17.5 mg/ml, 10 mg/ml, 5 mg/ml, 1 mg/ml

concentrations were prepared via serial dilution with a 5 mL Hamilton glass syringe.

For PEI or PVC, a stock solution was prepared in N-methyl-2-pyrolidine at a concentration

of 100 mg/ml by stirring overnight at a temperature of 50 °C and then passing the solution

through a 1 µm PTFE filter. Then solutions with 50 mg/ml, and 10 mg/ml concentrations for

PVC, and 100 mg/ml, and 10 mg/ml concentrations for PEI were prepared via serial dilution with a 5 mL Hamilton glass syringe.

Prior to spin-coating, silicon wafers were sequentially sonicated in deionized water containing alconox detergent (~ 1 mg/ml); neat, deionized water (MilliQ, <18MΩ); acetone; and isopropyl alcohol (for five minutes each) and then dried under nitrogen gas and cleaned with an air plasma in a Harrick plasma chamber at high power (18 Watts) for five minutes. Spin-coating (PWM32, Headway Research Inc., Garland, Texas) was performed both in a cleanroom to avoid contamination with dust particles and in a normal laboratory environment. Similar results were obtained from both sets of experiments. Films were cast by first coating the substrate with a liquid layer (2–3 mL) and then spinning them at a speed of 3000 RPM for two minutes, with a ramp of 100 RPM/s. After spin-coating, films were annealed in a vacuum oven at 160 °C for 12 hours. The only exception to this thermal annealing protocol was PVC, which was annealed at 60 °C to prevent thermal degradation, as indicated by discoloration in films annealed at higher temperature.

Measurements of Thickness. Thickness of films was determined by stylus profilometry (model, company, town, state) with a 12µm diamond tip (DektakXT, Bruker, Billerica, Massachusetts) at a normal force of 1 mg. A step edge was created in the center of the silicon wafer by scraping it with a razor blade. Reported values are the average of 7 independent measurements on the same wafer.

Density-based measurements using MagLev. MagLev were performed in aqueous solutions of manganese (II) chloride tetrahydrate of different concentrations for PS (2.3 M), PMMA (3.5 M), PVC (3.5 M), PEI (3.5 M), and PIBMA (3.5 M).

MagLev device specifications. The "axial MagLev" device uses two like-poles facing ring

magnets (NdFeB permanent magnets, OD × ID × H: 76.2 mm × 25.4 mm × 25.4 mm) positioned

coaxially with separation of 15.0 mm. The magnets were bought from kjmagnetics.com. The

magnets are fixed in 3D printed (Stratasys Fortus 250mc, Eden Prairie, MN) holders made of

acrylonitrile-butadiene-styrene-plastic (ABS) that were designed with the software

Solidworks^{TM}. Four threaded stainless-steel rods with hex nuts are used to hold the holders in

position. The ends of the stainless-steel rods are topped with cap nuts. A standard plastic cuvette

(45 mm in height) is used to levitate the diamagnetic samples in a paramagnetic medium

(aqueous solutions of $MnCl_2$ in all experiments reported here). The strength of the magnetic

field (0.33 T) was measured with a DC gauss-meter (Model GM1-ST; AlphaLab, Inc., Salt

Lake City, UT) at the center of the top face of the bottom magnet (N45 grade). See **Figure S10**

for a photograph of the MagLev device.

MagLev Measurement process. After cutting the 2" diameter wafer into ~0.25 cm^2 squares

using a diamond scribe, the sample was placed in the aqueous solution of $MnCl_2$—either directly

in the MagLev device, or in a cuvette outside of the MagLev device. After the sacrificial layer

dissolved, the film floated up to the surface if it was outside of the MagLev device or floated to a

stable levitation height if it was inside the MagLev device. The time for the delamination process

depended upon the material, thickness, and annealing protocol, and ranged from 1 minute to

several hours. When the solution containing the film was poured into the MagLev device, the

film floated to a stable levitation height. We found no difference in the measured density if the

film was delaminated inside or outside the MagLev device. We could not reliably measure films

< 3 nm thick because they were extremely delicate (*i.e.*, they broke into small pieces during the

delamination process) and were difficult to observe levitating in the paramagnetic medium.

Additionally, we found that the films delaminated more rapidly in deionized water and that the films released this way (and then transferred to the cuvette containing aqueous $MnCl_2$ solution) resulted in the same levitation height and thus value of density measured by MagLev.

FTIR-ATR analysis of polystyrene films and controls

The spin coated polystyrene films (~1 µm thick) and the controls (i.e., polystyrene pellets and films of PAA) were analyzed in their dry state at ambient conditions with Fourier transform infrared spectroscopy (FTIR-ATR Bruker Platinum, Bruker, Billerica, MA) with an attenuated total reflection (ATR) diamond window. We measured spectra between 4000–400 cm-1 at a resolution of 4 cm^{-1} with 64 sample and background scans (**Figure S7**).

S2. Tabulated Data
Table S1. Collated data from all the MagLev experiments done with PS films. In all cases, the solvent used was toluene.

Concentration (mg /mL) [†]	Spin speed (RPM)	Thickness (nm)*	Density (g/cm^3)
100.0	3000	1286±17	0.99±0.02
75.0	3000	395±11	1.03±0.02
50.0	3000	280±3	1.01±0.02
25.0	3000	150±6	1.07±0.04
17.5	5500	125±2	1.26±0.02
17.5	3000	127±5	1.25±0.04
17.5	500	377±3	1.01±0.02
10.0	3000	39±6	1.34±0.04
5.0	3000	13±4	1.52±0.03
1.0	3000	4±5	1.61±0.01

[†] We define concentration in mg/mL as 'mg of solid polymer per mL solvent'
* Thickness measured by stylus profilometry.

Table S2. Collated data from all the MagLev experiments performed with PMMA films. In all cases, the solvent used was toluene.

Concentration (mg/mL) [†]	Spin speed (RPM)	Thickness (nm)*	Density (g/cm^3)
100	3000	592±44	1.18±0.02
75	3000	478±30	1.14±0.02
55	3000	385±19	1.13±0.01
50	3000	226±7	1.12±0.01
25	3000	216±3	1.05±0.02
15	3000	68±6	0.87±0.02
10	3000	28±5	0.85±0.01
5	3000	9±4	0.76±0.02
1	3000	3±3	0.67±0.01

[†] We define concentration in mg/mL as 'mg of solid polymer per mL solvent'

* Thickness measured by stylus profilometry.

Table S3. Collated data from all of the MagLev experiments with PVC and PEI. In both cases, the solvent used was N-methyl-2-pyrolidine.

Polymer	Concentration (mg/mL) [†]	Spin speed (RPM)	Thickness (nm)*	Density (g/cm^3)
PVC	50	3000	526$\pm$8	1.38$\pm$0.01
PVC	10	3000	53$\pm$7	0.81$\pm$0.01
PEI	100	3000	1387$\pm$124	1.23$\pm$0.01
PEI	10	3000	17$\pm$3	1.52$\pm$0.01

[†] We define concentration in mg/mL as 'mg of solid polymer per mL solvent'
* Thickness measured by stylus profilometry.

S3. Calibration Curves
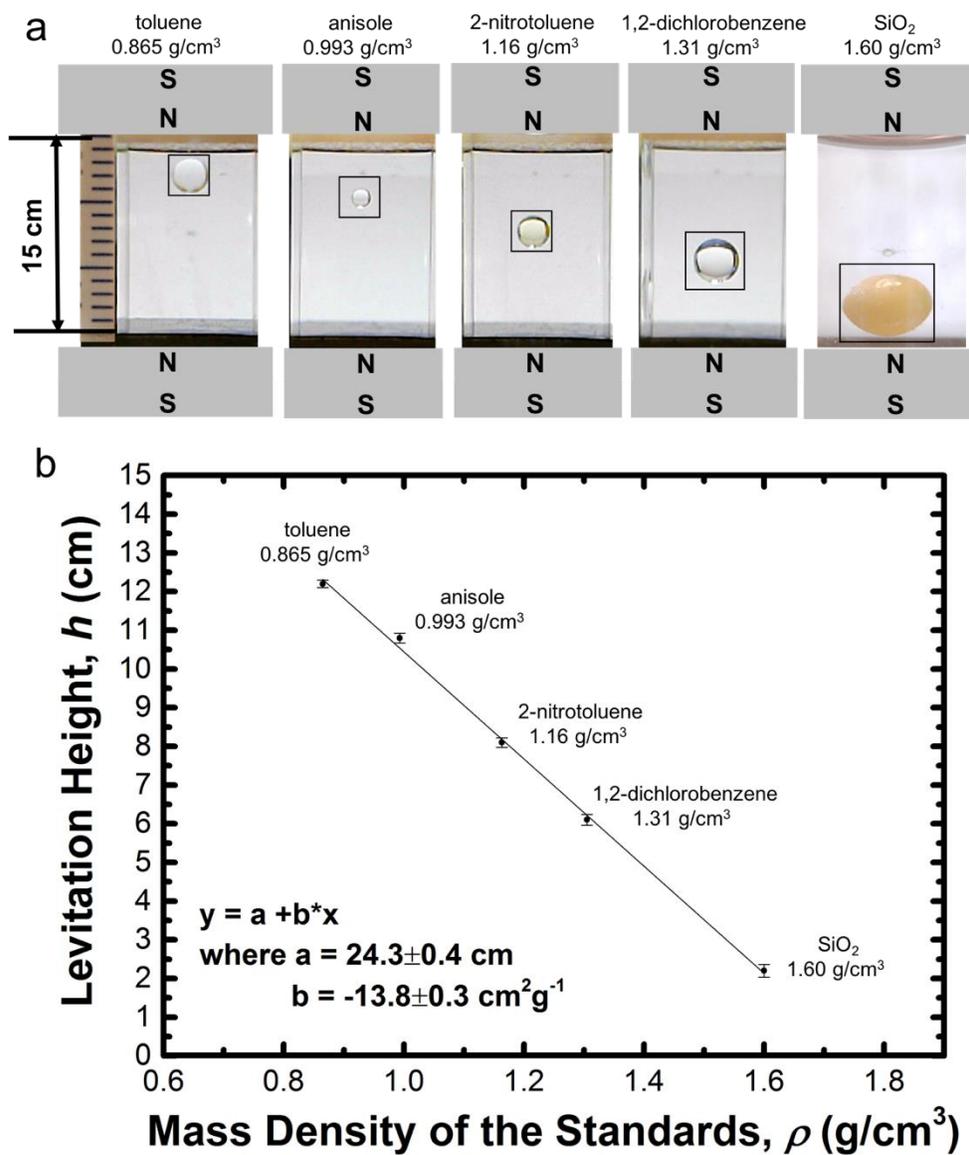
Figure S1. Calibration of axial magnetic levitation device with a 2.3 M solution of $MnCl_2$. (a)

Photographs of several density standards at different levitation heights. (b) Plot showing linear

correlation between levitation height and mass density. Organic liquids used to calibrate the

solution are toluene ($\rho = 0.865$ g/cm^3), anisole ($\rho = 0.993$ g/cm^3), 2-nitrotoluene ($\rho = 1.16$

g/cm^3), 1,2-dichlorobenzene ($\rho = 1.31$ g/cm^3), and SiO_2 bead ($\rho = 1.60$ g/cm^3).
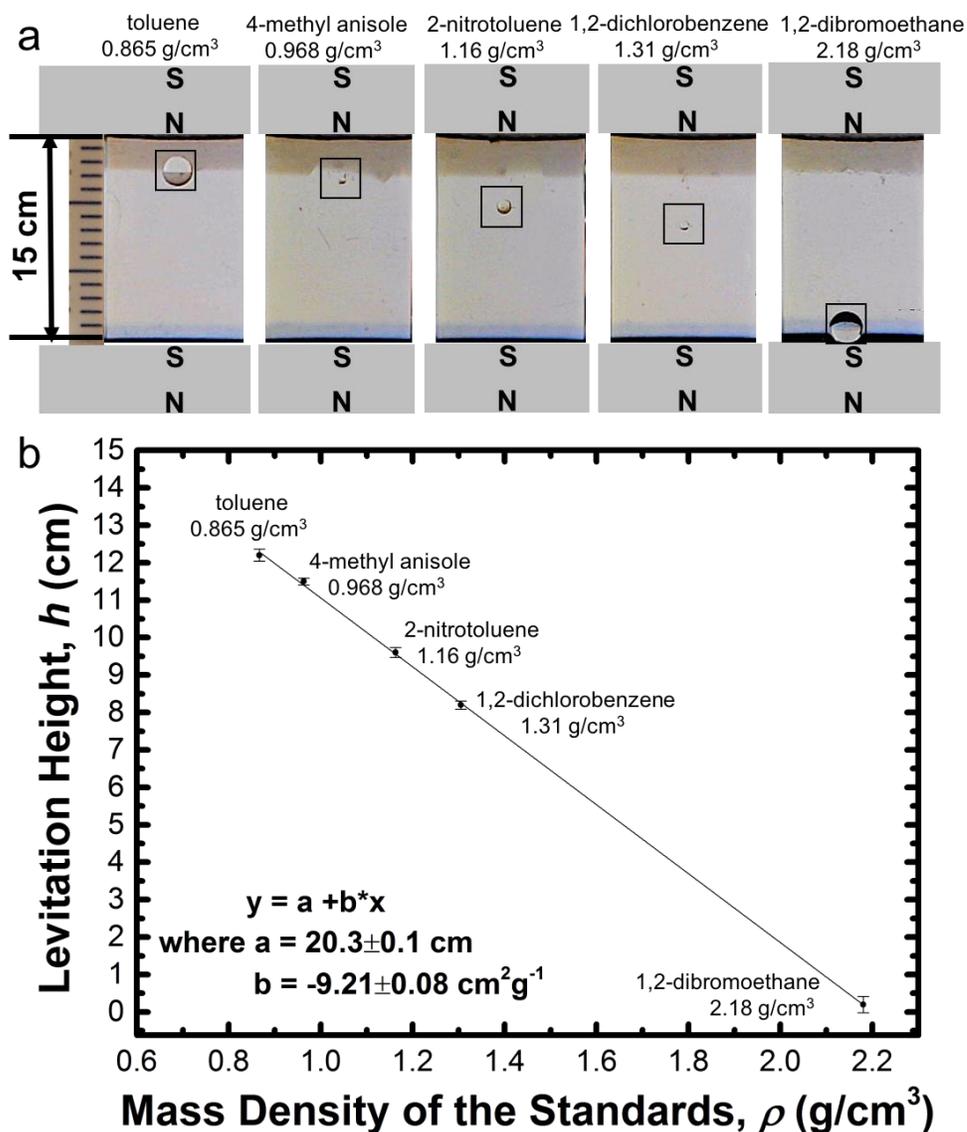
Figure S2. Calibration of axial magnetic levitation device with a 3.5 M solution of $MnCl_2$. (a) Photographs of several density standards at different levitation heights. (b) Plot showing linear correlation between levitation height and mass density. Organic liquids used to calibrate the solution are toluene ($\rho = 0.865$ g/cm^3), 4-methyl anisole ($\rho = 0.968$ g/cm^3), 2-nitrotoluene ($\rho = 1.16$ g/cm^3), 1,2-dichlorobenzene ($\rho = 1.31$ g/cm^3), and 1,2-dibromoethane ($\rho = 2.18$ g/cm^3).

S4. Supplemental Data
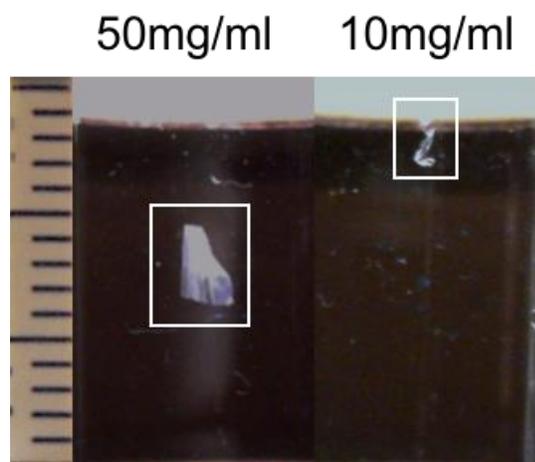
Figure S4. Photographs of thin films of PVC of varied thickness, magnetically levitating within the paramagnetic solution.
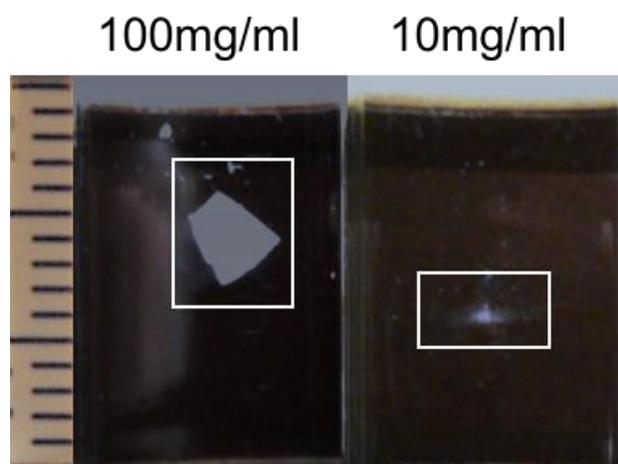
Figure S5. Photographs of thin films of PEI of varied thickness, magnetically levitating within the paramagnetic solution.
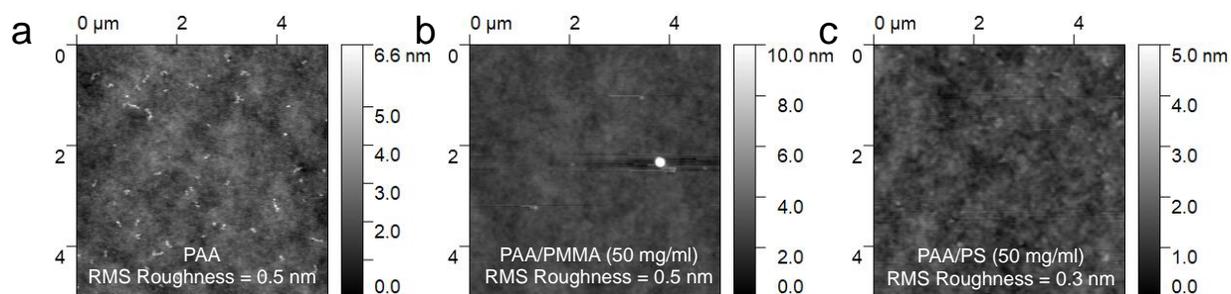
Figure S6. Atomic force microscopy (AFM) images of three representative films, confirming

that the root-mean-squared (RMS) roughness of each film was less than 1 nm. AFM images were

obtained using a Cypher microscope in tapping mode, with an AC200TS cantilever, from

Asylum Research, with a spring constant of 9 (N/m) and a resonant frequency of 100 – 200 kHz.

A scan window of 5x5 μm with a scanning frequency of 1Hz was employed. The RMS

roughness is defined mathematically as the root mean square average of the height deviations

from the mean height and was calculated from the raw data using the Gwyddion software

package.
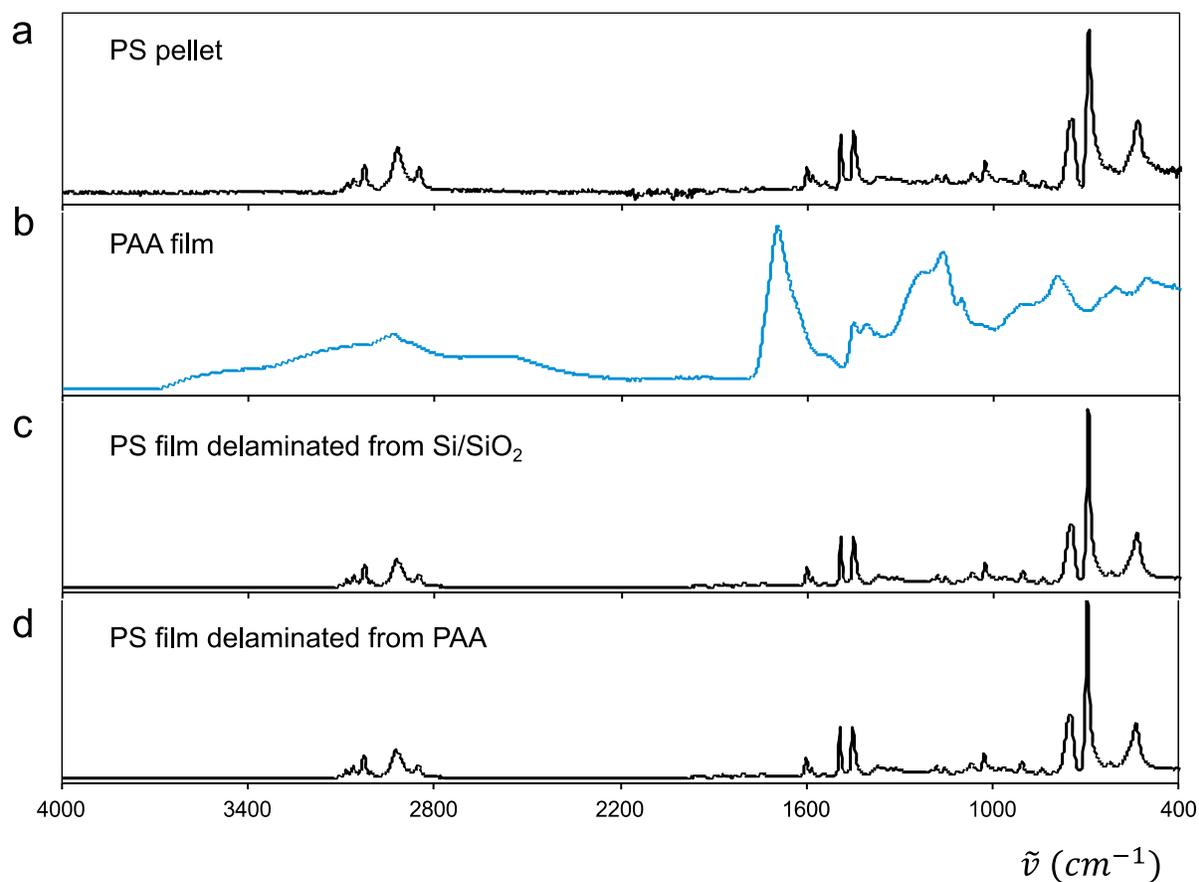
Figure S7. Attenuated total reflection Fourier transform infrared spectroscopy (FTIR-ATR) experiments showing no evidence of any PAA remaining on the PS film following delamination from the sacrificial layer. FTIR-ATR spectrum of (a) the PS pellet as received, (b) a film of PAA, (c) a film of PS delaminated from Si/SiO_2, and (d) a film of PS delaminated from PAA. The observation that the spectra in (c) and (d) are indistinguishable indicates that the concentration of PAA in the PS film must be less than the detection limit of 5-10 wt% for FTIR-ATR.

S4. Detailed Comparison to Prior Results

The density variations with thickness measured with MagLev qualitatively matched with previously reported measurements of PS and PMMA. For PS, the magnitude of the density variations measured in our experiments were larger than previously observed. These differences could in principle arise from i) differences in the polymer sample (i.e. molecular weight, and polydispersity), ii) differences in the substrate (i.e. strong attraction *vs.* weak attraction), and iii) systematic differences between the measurement techniques (i.e. reflectometry vs. buoyancy measurements). Regarding the polymer sample, we used a polydisperse sample of PS, whereas previous reports used monodisperse reference standards; the bulk density of our pellets was lower than the bulk density of the pellets employed in previous studies. Control experiments with a monodisperse sample, however, produced similar results.

We used PAA as a substrate, whereas previous studies employed a Si-H surface. The difference in attractive forces between these two surfaces could also be responsible for the larger magnitude of the effect measured in our experiments. Finally, our technique has a very different operating principle in comparison to reflectometry measurements and nanoparticle adsorption experiments. A key distinction between the observed values of density could be the surface roughness, which we measured to be slightly less than 1 nm in all cases. In both reflectometry and nanoparticle adsorption experiments, such a surface roughness could in principle alter the observed value of density—likely lowering the observed density due to the diffuseness of the surface. With our measurement it is unlikely that the surface roughness would result in a lowering of the observed density because that space could easily be filled in by the ionic paramagnetic solution and would play no role in the buoyancy force. In other words, the density that MagLev measures is that of the solvent-accessible volume of the film.
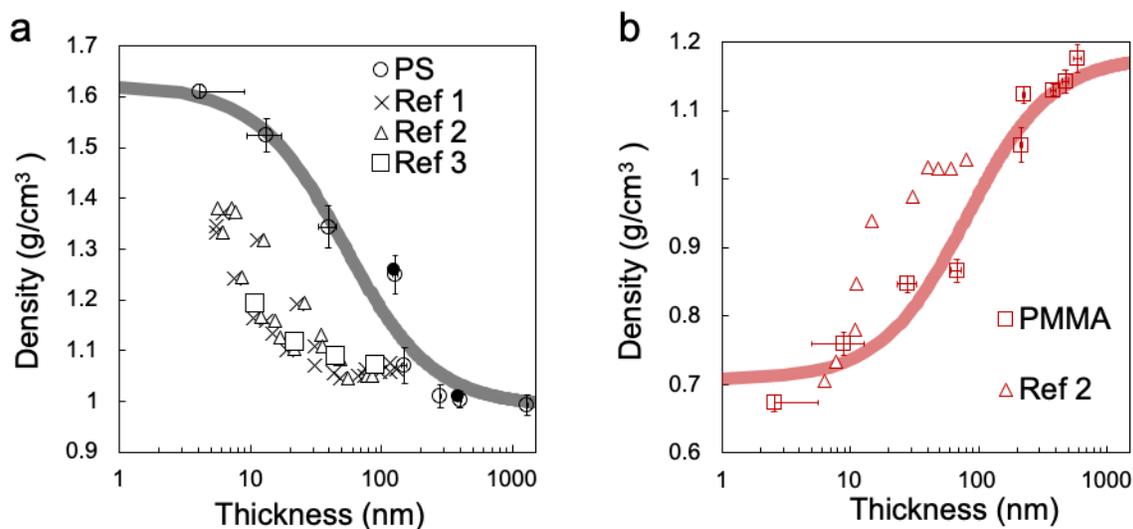
Figure S8. Comparison of density *vs.* thickness obtained by MagLev experiments with existing

data for (a) PS, and (b) PMMA. Data from reference 1 were obtained through the refractive

index, by a combination of XRR and ellipsometry. Data from reference 2 data were obtained

through the refractive index, by monitoring nanoparticle absorption. Data from reference 3 data

were obtained by molecular dynamics simulations. Solid lines are fits of our data to Eq. 1.
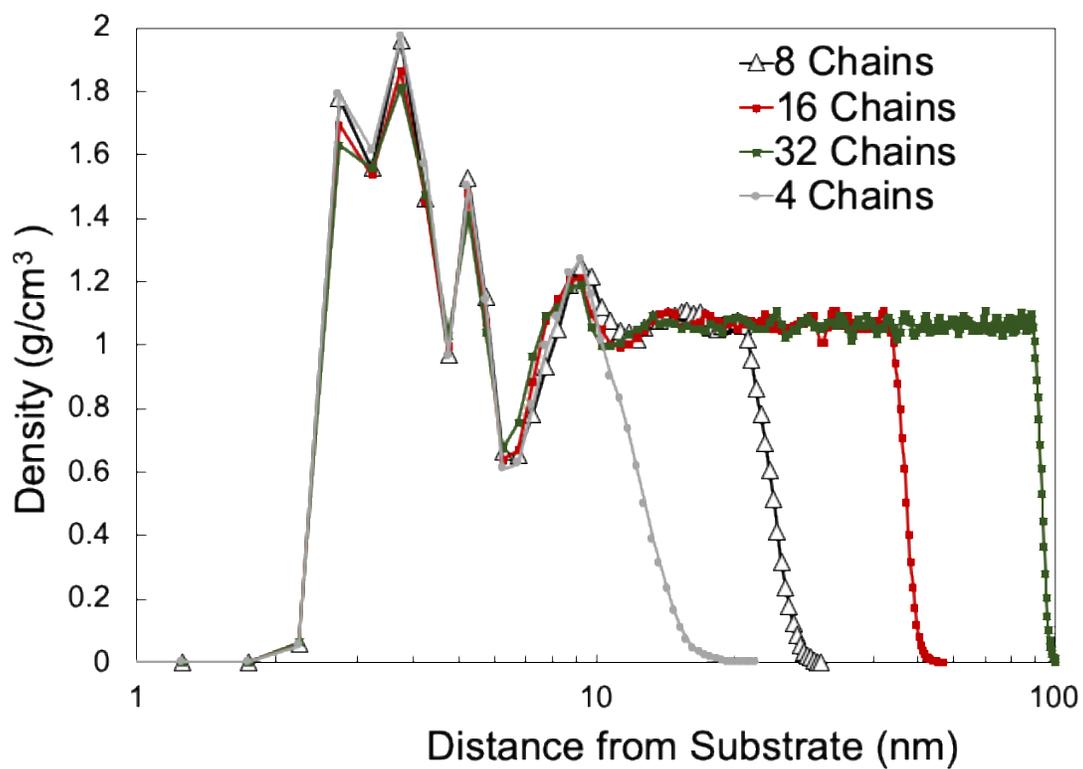
Figure S9. Density profiles in thin films of PS at 300K, reproduced from previously published molecular dynamics simulations (reference 3). These results show that an attractive substrate produces a densification up to almost 2 g/cm^3 at the buried interface with the substrate. These findings support the feasibility of the densification observed in MagLev experiments.
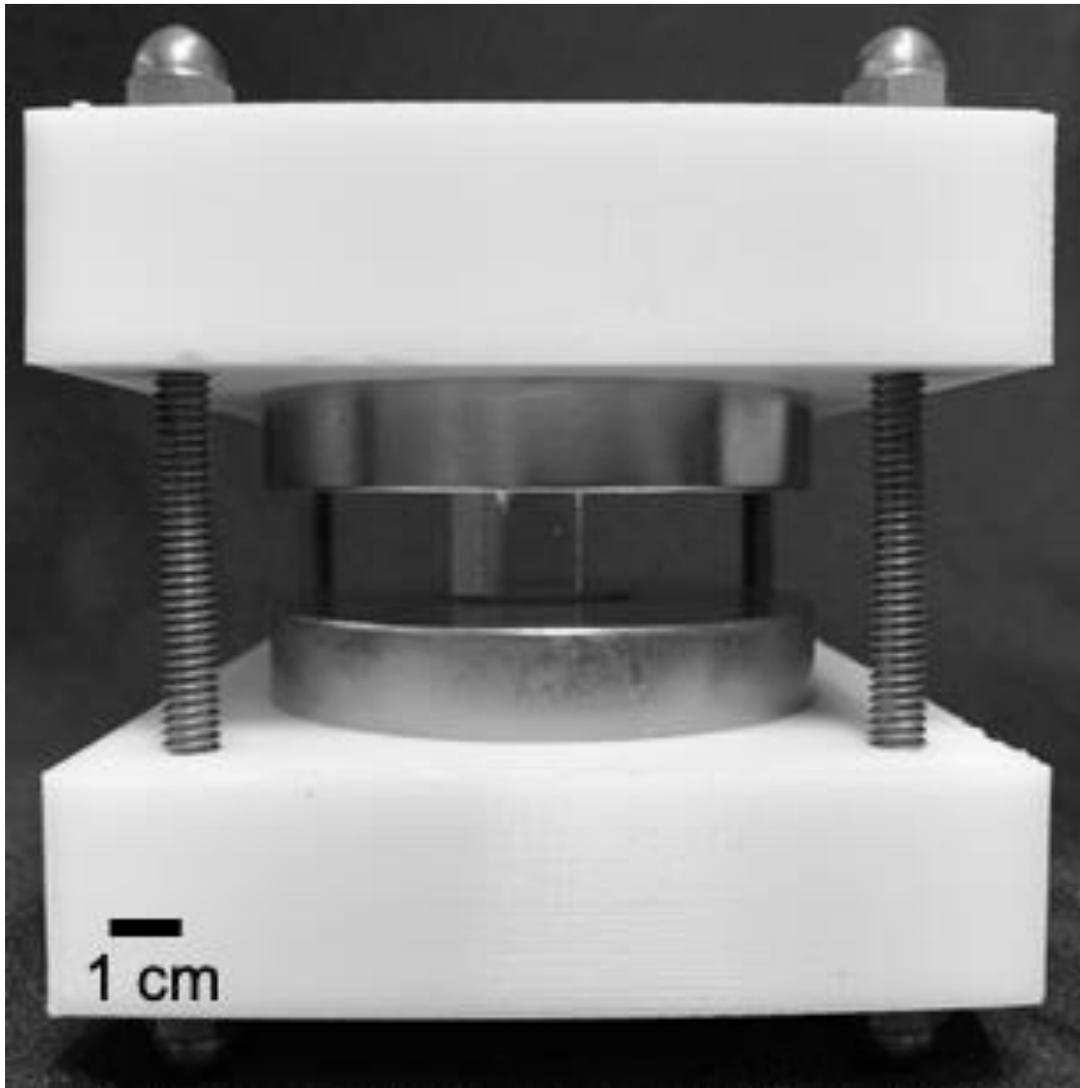
Figure S10. Photograph of the axial MagLev device used in all experiments.

References

1) Vignaud, G.; Chebil, M. S.; Bal, J. K.; Delorme, N.; Beuvier, T.; Grohens, Y.; Gibaud, A. Densification and Depression in Glass Transition Temperature in Polystyrene Thin Films. *Langmuir* **2014**, *30*, 11599–11608.

2) Unni, A. B.; Vignaud, G.; Chapel, J. P.; Giermanska, J.; Bal, J. K.; Delorme, N.; Beuvier, T.; Thomas, S.; Grohens, Y.; Gibaud, A. Probing the Density Variation of Confined Polymer Thin Films via Simple Model-Independent Nanoparticle Adsorption. *Macromolecules* **2017**, *50*, 1027–1036.

3) Hudzinskyy, D.; Lyulin, A. V.; Baljon, A. R. C.; Balabaev, N. K.; Michels, M. A. J. Effects of Strong Confinement on the Glass-Transition Temperature in Simulated Atactic Polystyrene Films. *Macromolecules* **2011**, *44*, 2299–2310.