

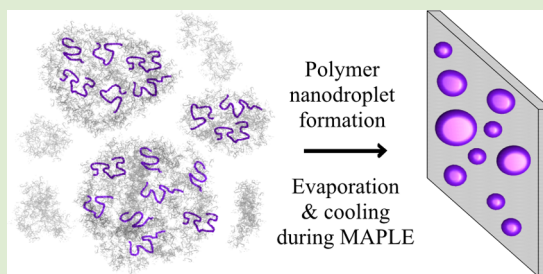
# Transport and Stability of Laser-Deposited Amorphous Polymer Nanoglobules

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## Supporting Information

**ABSTRACT:** We characterized the transport, i.e., time-of-flight, and nanoscale thermal properties of amorphous polymer nanoglobules fabricated via a laser-deposition technique, Matrix-Assisted Pulsed Laser Deposition (MAPLE). Here, we report the first experimental measurement of the velocity of polymer during MAPLE processing and its connection to nanostructured film formation. A nanoscale dilatometry technique using atomic force microscopy was employed to directly measure the thermal properties of MAPLE-deposited polymer nanoglobules. Similarly to bulk stable polymer glasses deposited by MAPLE, polymer nanoglobules were found to exhibit enhanced thermal stability and low density despite containing only thousands of molecules. By directly connecting the exceptional properties of the nanostructured building blocks to those of bulk stable glasses, we gain insight into the physics of glassy polymeric materials formed via vapor-assisted techniques.



Conceptually, glasses are liquids that have lost their ability to flow.<sup>1</sup> For millennia, the primary route to form vitreous materials has been rapid cooling from the liquid state.<sup>2</sup> If the liquid is cooled at high rates, crystal nucleation can be avoided, and the liquid becomes supercooled. Upon further cooling, molecular motions become progressively slower, and eventually, equilibrium is unattainable on the experimental time scale. The temperature at which the liquid falls out of equilibrium into the nonequilibrium glassy state on cooling is termed the glass transition temperature ( $T_g$ ). A result of the kinetic nature of glass formation is that  $T_g$ , density, and other key material properties can be tuned by varying the rate of cooling from the liquid. However, the use of supercooling to access glasses with dramatically different properties is limited. Varying the rate of cooling by one order-of-magnitude during quenching from the liquid state will result in only a  $\sim 3$ – $5$  K change in the value of  $T_g$  and a minute change in density.<sup>3</sup>

In an effort to overcome the kinetic limitations of glass formation and to facilitate control over the properties of disordered solid materials, the past few years have seen intense effort in the use of unconventional processing methodologies to form glasses. In a seminal study, Ediger and co-workers demonstrated that organic molecular glasses formed via slow physical vapor deposition (PVD) exhibited exceptional kinetic and thermal stability.<sup>4</sup> Termed “stable” glasses, these materials were characterized by a  $\sim 15$  K increase in the onset temperature of the glass transition ( $T_{\text{onset}}$ ) during heating, 2% greater density, and  $\sim 8$  J/g lower enthalpy compared to an analogous glass formed via supercooling. By all accounts, stable glass formation is a general phenomenon for organic small molecules suitable for PVD. The diversity of materials that have been transformed into stable glasses via PVD includes

indomethacin, trisnaphthylbenzene and isomers, decalin, and toluene.<sup>4–7</sup>

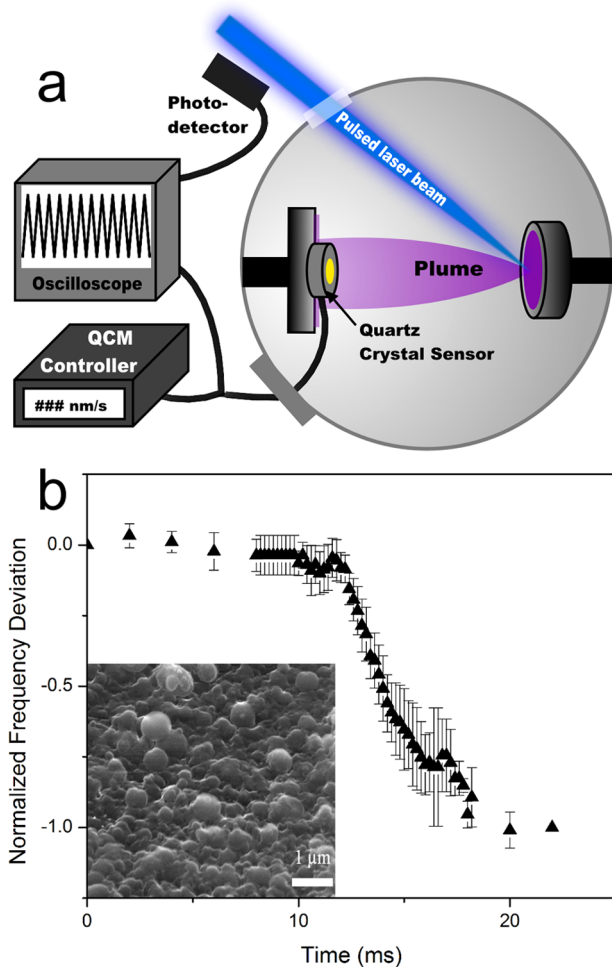
Recent work has focused on the challenge of expanding the range of materials that can be transformed into stable glasses, with particular focus on those that are not amenable to PVD processing. These include both metallic<sup>8,9</sup> and polymeric<sup>10</sup> glasses. Here, we focus on stable polymer glasses formed via Matrix-Assisted Pulsed Laser Deposition (MAPLE), a versatile vapor-assisted deposition technique by which films of polymers, proteins, small molecules, and nanoparticles can be fabricated.<sup>11–14</sup> In the MAPLE process, thin films of macromolecules can be grown at slow rates, i.e., less than 1 nm/s. Stable polymer glasses formed via MAPLE exhibit significantly enhanced  $T_{\text{onset}}$  and improved high-temperature kinetic stability relative to glasses formed via supercooling. Both these characteristics are in accord with organic small molecule stable glasses. In contrast with small molecule stable glasses, stable polymer glasses uniquely have  $\sim 30$  J/g higher enthalpy and dramatically reduced density (40%).<sup>10</sup> This unusual combination of material properties is only realized when MAPLE-deposited polymer glasses exhibit a novel nanostructured morphology, as illustrated in the Figure 1b inset.

In our prior work, we explored the origins of nanostructured film formation via MAPLE.<sup>15,16</sup> As confirmed by Atomic Force Microscope (AFM) topology images and Scanning Electron Microscope (SEM) cross-sectional images, stable polymer films prepared by MAPLE are formed by the assembly of intact

**Received:** September 2, 2014

**Accepted:** September 30, 2014

**Published:** October 2, 2014



**Figure 1.** (a) Schematic of MAPLE, equipped with a time-of-flight (TOF) system. (b) Normalized deviation of the quartz crystal sensor frequency vs time after the laser ablates the target. Inset: SEM image of a MAPLE-deposited PMMA bulk film.

nanoglobules consisting of  $10^1$  to  $10^5$  polymer molecules.<sup>15</sup> However, the conditions under which polymer nanoglobules may impact the substrate without damage or disintegration remain an open question. The investigation of surface nanoglobule coalescence in bulk films as a function of deposition temperature demonstrated that nanoscale features persist well above the material's standard  $T_g$ , indicating that enhanced stability is present at the nanoscale.<sup>16</sup> However, because these experiments examine structure at the surface of a bulk film, this measurement of nanoscale stability is indirect. To conclusively attribute the measured macroscopically enhanced stability to the material's nanoscale morphology, a direct measurement of the thermal properties of individual nanoglobules is warranted. Such study is necessary to obtain a better understanding of the relationship between material properties at the nano- and macroscales of MAPLE-deposited glassy films. In this letter, we address two major questions related to polymer stable glass formation. First, to understand how nanoglobules remain intact after transport and deposition onto the substrate (or growing film), we report for the first time, the measurement of the time-of-flight and average velocity of material during MAPLE processing. Second, we directly investigate the nanoscale thermal stability of isolated nanoglobules via AFM. Combined, these two novel characterizations

will allow us to relate the bulk and nanoscale material properties to the physics of the laser-deposition process. Because the combination of bulk properties observed in our material is unique (enhanced stability, low density, and high enthalpy), a better understanding of the nanoscale properties of these glasses provides insight into the physics of amorphous materials prepared via vapor-assisted deposition.

As opposed to direct polymer ablation, MAPLE provides a gentler mechanism for the deposition of polymer films with thicknesses ranging from a few nanometers to microns.<sup>11</sup> In the technique, a pulsed laser ablates a target consisting of a frozen dilute solution of the desired polymer producing thin films of the material.<sup>12,13</sup> The mechanism of film growth has recently been refined by insight obtained via simulations performed by Zhigilei and co-workers.<sup>17–20</sup> They provided evidence that polymer molecules are ejected from the target within polymer–solvent clusters. These clusters form due to explosive decomposition of the solvent molecules when a short laser pulse superheats the target beyond the ablation threshold. During transport from target to substrate, solvent is rapidly removed from the clusters, forming polymer nanoglobules.<sup>15</sup> Simulations revealed that depending on a nanoglobule's velocity upon impact with the substrate it may remain intact or disintegrate into polymer fragments.<sup>20</sup> It was illustrated that polymer nanoglobules with velocities less than 100 m/s do not lose structural integrity upon impact with the substrate. Yet, the velocity of ejected nanoglobules during the MAPLE process has not been experimentally measured to confirm how nanoglobules can deposit intact without coalescence.

Figure 1a shows a schematic of the MAPLE setup equipped with a custom-built time-of-flight (TOF) system based on a quartz crystal microbalance (QCM). Isolated nanoglobules of poly(methyl methacrylate) (PMMA) were deposited from a chloroform target solution, and TOF was measured by tracking the deviation of the quartz crystal frequency in real time as the nanoglobules arrived at the crystal surface. A detailed experimental protocol is provided in the Supporting Information (SI). Figure 1b shows the normalized QCM oscillation frequency as a function of time after laser ablation of the target. Deviation from the initial steady-state frequency began at  $\sim 10$  ms, thus indicating the arrival of the first measurable portions of the plume to the sensor. The distance between the sensor and target was set to  $\sim 5$  cm, yielding an average velocity of  $\sim 5$  m/s for depositing material. This value is significantly lower than the threshold velocity (100 m/s) required for structural integrity of the depositing nanoglobules upon impact with the substrate. Because this velocity measurement is conducted at the process conditions under which bulk stable glasses are formed by MAPLE, we demonstrate that the formation of bulk stable glasses is made possible by the low impact velocity of depositing nanoglobules.

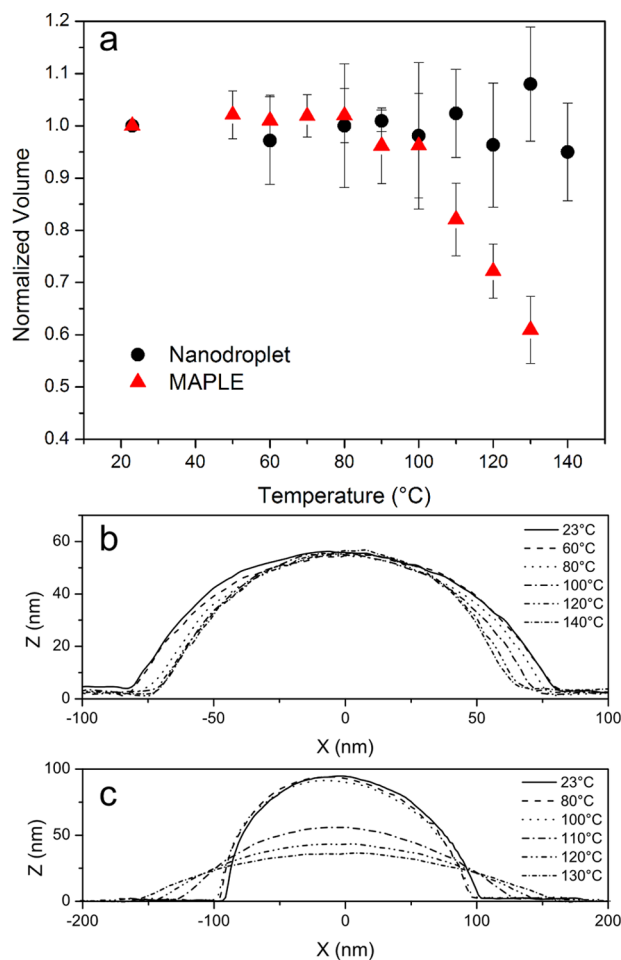
In comparison with velocity measurements made on other laser-material transfer techniques, such as MALDI, Pulsed Laser Deposition, and Laser-Induced Forward Transfer (LIFT), our measured velocity is low. Direct laser ablation of PMMA results in a velocity of 200 m/s, with a fluence (energy per area)  $4\times$  higher than that used in this study.<sup>21</sup> Studies of LIFT of live cells<sup>22</sup> and hydrogels<sup>23</sup> reported velocities of 122 and 66 m/s, respectively. The low velocity reported for MAPLE-deposited material may be attributed to a combination of many factors. Neutral species travel more slowly than ionized species,<sup>24</sup> and larger material clusters travel more slowly than small clusters.<sup>25</sup> MAPLE-deposited polymer is neutral and deposited in clusters

of large numbers of molecules at fluence near the ablation threshold, resulting in low transport velocity. Though the techniques are similar, in the MALDI process, where species are both ionized and in small clusters, much higher velocities on the order of kilometers/second are frequently observed.<sup>24</sup> The low velocity of the deposited material shows that, despite laser ablation, MAPLE deposition under these process conditions is gentle with respect to kinetic energy.

In the initial work, we extensively characterized the bulk properties of stable glassy PMMA which forms by the assembly of intact polymer nanoglobules.<sup>10</sup> We have subsequently suggested that the unique combination of high thermal stability and low density observed in the bulk results from processing history imposed by MAPLE.<sup>16</sup> Here, we directly address the question of the building blocks' thermal stability and density via nanoscale dilatometry. We investigated the thermal properties of individual PMMA nanofeatures with two different processing histories: isolated nanoglobules made by short-time MAPLE deposition and model nanodroplets formed from annealed nanoparticles. Using our nanoscale dilatometry technique, the volume of individual nanoglobules/droplets was tracked over a range of temperatures via heated AFM (see SI for detailed preparation conditions and experimental protocol). We focus on nanoglobules and nanodroplets with volumes similar to the characteristic size of features in stable nanostructured bulk films ( $>10^{-21} \text{ m}^3$ ).

Figure 2a plots the normalized volume vs temperature measured on heating for as-deposited nanoglobules and model nanodroplets. The nanoglobules and nanodroplets were sufficiently equilibrated at each temperature step such that the measurements are time-independent. As illustrated in Figure 2a, the volume of the model nanodroplets did not change upon heating from room temperature to 140 °C, within the resolution of the technique. Volume changes due to thermal expansion ( $<1\%$ ) are hidden within the error bars. The MAPLE-deposited nanoglobules exhibit a dramatically different thermal response upon heating. At  $\sim 110$  °C, the onset of a reduction in nanoglobule volume is observed. Further heating results in a precipitous drop in volume such that at 130 °C the volume has decreased by  $\sim 40\%$  compared to its initial value. Figures 2b and 2c illustrate cross-sectional (XZ) profiles obtained via AFM of a PMMA nanodroplet and nanoglobule, respectively, upon heating. The profile of the model nanodroplet remains approximately constant upon heating to 140 °C. In contrast, the profile of the as-deposited nanoglobule remains unchanged upon heating only to 100 °C. Additional heating results in a reduction in nanoglobule height and broadening in diameter.

We interpret the above results in the context of the materials' processing histories. Model nanodroplets, which were formed by cooling from the liquid state, have a  $T_g$  of  $\sim 100$  °C. Upon heating, minute increases in volume due to thermal expansion were not detectable within the resolution of AFM; hence a dilatometric  $T_g$  could not be observed upon heating, and thus constant volume was observed. The constant-volume measurement also confirms there is no significant diffusion of polymer molecules into or out of the droplet during the experiment. MAPLE-processed nanoglobules are prepared from PMMA with a standard  $T_g$  value of  $\sim 86$  °C. We demonstrated that the MAPLE route to the vitreous state trapped macromolecules into a high-energy, low-density state.<sup>10</sup> We observe that only upon heating the nanoglobules to 110 °C do the macromolecules obtain sufficient mobility that the excess volume can

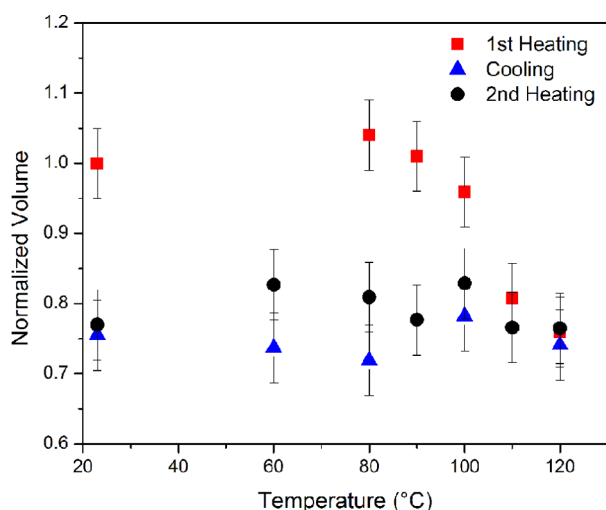


**Figure 2.** (a) Normalized volume of polymer nanodroplets and MAPLE-deposited nanoglobules as a function of temperature for large features ( $V > 10^{-21} \text{ m}^3$ ). (b) Profiles of a large nanodroplet's XZ cross-section as it is heated. (c) Profiles of a large MAPLE-deposited nanoglobule's XZ cross-section as it is heated.

begin to relax. The total loss in volume at 130 °C is  $\sim 40\%$ . Two main points are deduced from these observations. First, the temperature at which the macromolecules obtain sufficient mobility for structural relaxation is  $\sim 25$  K greater than the standard  $T_g$ . This provides compelling evidence that the enhanced thermal stability measured in bulk is directly related to enhanced nanoscale stability. Second, the reduction in volume observed on heating an isolated nanoglobule is nearly equal to the density change observed between bulk MAPLE-deposited and standard films.<sup>10</sup> Hence, the dramatically reduced density observed in bulk MAPLE films cannot be attributed to interstitial volume due to packing of nanoglobules but to the properties of the nanoglobules and the molecules of which they are composed. Thus, we have shown that MAPLE-deposited nanoglobules are both stable and low-density, like their bulk counterparts, despite containing only 1000s to 100 000s of polymer molecules.

Bulk stable MAPLE-deposited films transform into standard glasses after sufficient annealing above  $T_g$  to erase prior thermal history. This transformation was tested at the nanoscale using isolated MAPLE-deposited nanoglobules. Figure 3 shows the behavior of a MAPLE-deposited nanoglobule during thermal cycling, subjected to heating, cooling, and reheating scans. On initial heating (represented by squares), a dramatic reduction in





**Figure 3.** Normalized volume of a MAPLE-deposited nanoglobule as it is heated, cooled, and reheated during atomic force microscopy measurements.

volume is observed. A subsequent cooling step to room temperature results in no change in volume, as illustrated by the triangles. After annealing at ambient conditions for 12 h, volume was measured on reheating. As demonstrated by the circles in Figure 3, no change in volume was observed on second heating in comparison to that obtained on the cooling cycle, within error. Similarly to bulk films, nanoglobules prepared by MAPLE also exhibited a transformation from a stable to standard polymer glass after the MAPLE thermal history was erased. This experiment also shows that the large decrease in nanoglobule volume is not an artifact of the measurement process.

The low density of MAPLE-deposited polymer nanoglobules is remarkable in that it is an order of magnitude larger than typical changes in glass density (<1% for thermal expansion, 2–3% for ultrastable small molecule glasses). It is important to consider potential molecular configurations inside the nanoglobule which could accommodate 40% excess volume. According to Zhigilei's simulations of MAPLE-deposited polymer/solvent clusters,<sup>19</sup> under certain conditions, clusters form a polymer-rich shell with a hollow center, termed a molecular balloon. Though a molecular balloon could easily include 40% empty volume, based on our experimental observations, we do not believe that the MAPLE-deposited polymer nanoglobules are hollow. In Zhigilei's work, "deflated balloon" structures are consistently observed,<sup>19,26</sup> acting as experimental confirmation of a hollow structure, which we do not observe in our experiments. Instead, it is likely that much smaller pockets or nanopores of excess volume are distributed throughout the nanoglobule facilitated by chain stretching. During transport from target to substrate, the nanoglobule undergoes rapid cooling ( $>10^6$  K/min<sup>16</sup>) and solvent stripping (0.5% to >50% polymer in under 10 ms<sup>20</sup>). Due to this rapid change in concentration, polymer chains may become kinetically trapped in the extended configurations characteristic of a polymer in good solvent, locking in excess volume and energy. In studies of the bulk MAPLE-deposited PMMA, 30 J/g excess enthalpy is reported at 340 K. This corresponds to  $O(10^{-19})$  J per polymer chain, or  $\sim 150$  kT, consistent with the suggestion that chains inside the nanoglobules are trapped in stretched configurations. For reference, if we assumed strong extension

along the main chain backbone, the Langevin function estimates that the average end-to-end distance would be  $\sim 90\%$  of the maximum value. Additionally, in the literature, it has been reported that glasses formed by concentration jumps exhibit enhanced stability on heating and excess volume.<sup>27</sup> Though the excess volume reported by McKenna is still an order of magnitude lower than that observed here, the rate of the change in concentration is likely much higher in the MAPLE process. In ongoing work, we are applying experimental techniques to assess the size scale of the excess volume in the nanoglobules.

In this work, we applied novel techniques to characterize the transport and nanoscale properties of laser-deposited polymer glasses. We showed, via the first experimental measurement of time-of-flight during MAPLE deposition, that the piece-wise assembly of bulk nanostructured glasses is made possible by the low velocity of depositing polymer nanoglobules during processing. To understand the exceptional properties observed in bulk ultrastable nanostructured glasses fabricated by MAPLE, we directly measured the thermal properties of the nanoglobule building blocks, using heated AFM. Laser-deposited nanoglobules exhibit a 40% decrease in volume upon heating, while control polymer nanodroplets show no volume change. This suggests the presence of excess volume in the nanoglobules at room temperature, in good agreement with density measurements of bulk MAPLE films. The laser-deposited nanoglobules also demonstrate enhanced stability, with no significant loss in volume occurring until  $\sim 25$  K above the bulk material's glass transition temperature. The exceptional thermal stability and decreased density observed in bulk ultrastable glasses can therefore be directly attributed to the polymer nanoglobules' nanoscale properties. Through these experiments, we provide insight into the nanoscale physics of glassy materials formed by MAPLE and the relationship between bulk and nanoscale properties of stable polymer glasses.

## EXPERIMENTAL SECTION

A KrF excimer laser (LightMachinery,  $\lambda = 248$  nm) with 20 ns pulses was used for all depositions (Fluence =  $0.125$  J/cm<sup>2</sup>; pulse rate = 5 Hz), and 0.1% by weight PMMA in chloroform was used as the target material for isolated nanoglobule depositions (2.5 or 5 min) and 1% solution for time-of-flight measurements. AFM analysis was performed on a Digital Instruments Nanoscope IIIa Multimode AFM in Tapping Mode, equipped with a controlled heating stage. The time-of-flight measurement system was constructed utilizing a 6 MHz Quartz Crystal Microbalance system (Lesker FTM-2400 with single sensor) and a GaP photodetector (ThorLabs 150–550 nm).

## ASSOCIATED CONTENT

### Supporting Information

The SI contains detailed experimental information for the time-of-flight system, preparation of isolated nanoglobules by MAPLE, and preparation of control nanodroplets. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We acknowledge support of the National Science Foundation (NSF) Materials Research Science and Engineering Center program through the Princeton Center for Complex Materials (DMR-0819860) and usage of the PRISM Imaging and Analysis Center at Princeton University. R.D.P. acknowledges partial support from the NSF through a CAREER Award (DMR-1053144) and the AFOSR through a YIP Award (FA9550-12-1-0223).

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