Ultrastable nanostructured polymer glasses

Nuclear Magnetic Resonance (NMR). NMR spectra of original and MAPLE-deposited PMMA \( (T_{\text{substrate}} = 336 \text{ K}) \) dissolved in deuterated chloroform (CDCl\(_3\)) were obtained by using a Bruker 500MHz, cryo-\(^1\text{H}\) optimized NMR spectrometer. Figure S1 shows the NMR spectra of PMMA before and after MAPLE deposition. Both spectra show identical structures of PMMA, which provides evidence that the MAPLE process did not destroy chemical bonds in PMMA.

Figure S1. (A) Detailed \(^1\text{H}\) NMR spectra of original PMMA and (B) MAPLE deposited PMMA.
Fourier Transform Infrared Spectroscopy (FTIR). FTIR transmission spectra were measured by a N$_2$-purged Nicolet 8700 FTIR spectrometer with a MCT detector. Spectral resolution was 4 cm$^{-1}$ and 20 scans were repeated for each measurement. The substrate used for FTIR measurement was a Si (1 0 0) test wafer purchased from Silicon Quest International Inc. Water and CO$_2$ traces were removed from the raw data and baseline correction was performed to compare the results of PMMA before and after MAPLE deposition. From Figure S2, we identified the same transmission peak positions for both PMMA films. The MAPLE sample was prepared at 311 K, while the ordinary PMMA film was spin-coated from 5 wt% toluene solution at 1000 rpm for 1 min.

![Figure S2](image.png)

**Figure S2.** FTIR spectra of PMMA films from spin coating and MAPLE.

Gel Permeation Chromatography (GPC). Weight-average molecular weight ($M_w$) was measured by GPC (Waters 515 HPLC pump, Eppendorf CH-460 column heaters, Waters 410 differential refractometer). As shown in Figure S3, no degradation occurred during MAPLE deposition.
Figure S3. Molecular weight of original and MAPLE-deposited PMMA measured by GPC. Original PMMA: $M_w = 14.94 \times 10^3 \text{ g/mol}$, PDI = 1.842; MAPLE-deposited PMMA: $M_w = 14.36 \times 10^3 \text{ g/mol}$, PDI = 1.816.

**X-Ray Reflectivity (XRR).** XRR measurements were applied to determine the density of PMMA films prepared by spin coating and MAPLE. Experimental setup of XRR was very similar to that in WAXS tests. In XRR, a knife-edge was placed very close to the sample surface to reduce the irradiated area for sufficient angular resolution. 0.2-mm-wide slits were mounted on both the X-ray source side and the detector side. In the XRR scan, the $2\theta$ diffraction angle range was $0 - 1^\circ$, and the scan speed was 0.1 sec/step, with an angle increment of 0.005°. Figure S4 shows the X-ray reflectivity data of PMMA films from both spin coating and MAPLE deposition. The critical angle of incidence $\alpha_c$ is related to material density ($SI$):

$$\rho_{el} = \frac{\alpha_c^2 \pi}{\lambda^2 r_{el}}$$

where $\lambda = 0.154 \text{ nm}$, $r_{el}$ is the classical electron radius, $r_{el} \approx 2.82 \times 10^{-15} \text{ m}$ ($SI$), $\rho_{el}$ is the mean electron density, which is related to the mean mass density of the material by:

$$\rho_{m} = \frac{\rho_{el} A}{N_A Z}$$
where \( N_A \) is the Avogadro constant, \( A \) is the mass number, \( Z \) is the atomic number. For PMMA film on Si wafer, there are two critical angles (change of the curve derivative) detected on reflectivity curve. In Figure S4, \( \alpha_{c2} \) and \( \alpha_{c4} \) are the response of Si substrate, and \( \alpha_{c1} \) and \( \alpha_{c3} \) are from the PMMA films. Combining equations (1) and (2), for a specific material, the critical angle \( \alpha_c \) is proportional to the square root of material density \( \sqrt{\rho_m} \), i.e., \( \alpha_c = C \sqrt{\rho_m} \), where \( C \) is a constant. Therefore, the density of PMMA films can be determined from their critical angle data. By setting the density of PMMA from spin-coating to 1.19 g/cm\(^3\), the value reported in Ref. S2, the density of MAPLE-deposited PMMA \( \rho_{PMMA-MAPLE} \) was found to be 0.742 g/cm\(^3\). Therefore, the MAPLE-deposited PMMA was \( \sim 37.6 \pm 1.85\% \) lighter than the ordinary PMMA. The critical angles of PMMA by spin-coating and MAPLE were 0.187±0.0013° and 0.147±0.0015°, respectively.

**Figure S4.** X-ray reflectivity of (A) spin-coated and (B) MAPLE-deposited PMMA \((T_{\text{substrate}} = 311 \text{ K}, \text{ deposition rate} = 0.25 \text{ nm/sec})\) films on Si (100) substrate.
**Refractive Index (RI).** The density of polymer films was also identified from the RI data through the Lorentz-Lorenz equation. RI measurements were performed using a single wavelength ellipsometer Gaertner Scientific LS116S300. The wavelength was 632.8 nm. According to the Lorentz-Lorenz equation, density of polymer film is given by (S3)

\[ L = \frac{(n^2 - 1)}{(n^2 + 2)} = \rho C \]

where \( L \) is defined as the Lorentz-Lorenz parameter, \( n \) is the RI, \( C = N_\alpha \alpha / 3 M_0 \varepsilon_0 \) which may be assumed to be constant for PMMA films prepared by spin-coating and MAPLE. \( N_\alpha \) is Avogadro’s number, \( M_0 \) is the molecular weight of the polymer repeat unit, and \( \varepsilon_0 \) is the electric constant. The density of spin-coated PMMA was determined to be 1.184 g/cm\(^3\). Thus, the constant \( C \) could be determined and then applied to MAPLE-deposited films. The density of the MAPLE-deposited PMMA (\( T_{substrate} = 311 \) K, deposition rate = 0.25 nm/sec) by RI was determined to be 0.681 g/cm\(^3\), which is ~ 42% less than ordinary PMMA.

**Atomic Force Microscopy (AFM).** The morphological property of MAPLE-deposited PMMA film was investigated by atomic force microscopy (Digital Instruments Multimode AFM, used in tapping mode). 5 x 5 \( \mu \text{m}^2 \) areas at three different positions were scanned on the film.

**Scanning Electron Microscopy (SEM).** The cross-sectional SEM images of MAPLE-deposited PMMA films were taken from a freshly broken glass-supported sample mounted almost vertically (tilted by 15°). The breaking process itself was carried out at room temperature by scratching an edge of the substrate and subsequent breaking over a wedge. Hence the interface remained untouched, representing the original state inside the sample now observable in cross-section. The prepared film was characterized on a LEO Gemini 1530 microscope (Carl Zeiss AG, Oberkochen, Germany) with acceleration voltage of 0.7 kV in secondary electrons InLens detection mode.
Supplementary References

