Supporting Information for: Relaxation Dynamics of thin Matrimid® 5218 Films in Organic Solvents

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SPECTROSCOPIC ELLIPSOMETRY

To determine the optical model for matrimid, different optical models were compared for a dry matrimid sample. In Table S1, an overview of the outcomes of the different optical models is presented.
Table S1. Overview of the different optical models and their fit parameters for 5 random spots on a dry matrimid sample. The error margins indicate the standard deviation. #Fit indicates the number of fit parameters used in the optical model, RMSE is the root mean squared error for the fit, $n_o$ is the ordinary refractive index determined at 632.8 nm, $k$ is the Urbach absorption tail amplitude, $dzA$ is the difference parameter between the ordinary and extraordinary A fit parameter of the Cauchy dispersion and %grading represents the thickness inhomogeneity perpendicular to the substrate.

| Model choice: | #Fit | RMSE  | Thickness (nm) | $n_o$ at 632.8 nm | $k_{amplitude}$ | $dzA$ | %grading |
|---------------|------|-------|----------------|-------------------|-----------------|-------|----------|
| $d$, Cauchy $A$, $B$, $C$ | 4    | 21.9 ± 0.4 | 256.5 ± 0.5 | 1.6478 ± 0.0009 |                  |       |          |
| $d$, Cauchy $A$, $B$, $k$ | 4    | 10.0 ± 0.2 | 263.5 ± 0.5 | 1.6175 ± 0.0006 | 0.0094 ± 0.0002 |       |          |
| $d$, Cauchy $A$, $B$, $C$, $k$ | 5    | 8.5 ± 0.1 | 263.3 ± 0.4 | 1.6192 ± 0.0005 | 0.0093 ± 0.0001 |       |          |
| $d$, Cauchy $A$, $B$, $k$, $dzA$ (anisotropy) | 5    | 9.8 ± 0.2 | 263.5 ± 0.5 | 1.6175 ± 0.0006 | 0.0093 ± 0.0002 | -0.0023 ± 0.0002 |          |
| $d$, Cauchy $A$, $B$, $C$, $dzA$ (anisotropy) | 5    | 19.3 ± 0.6 | 257.3 ± 0.5 | 1.6484 ± 0.0009 |                  | -0.0167 ± 0.0003 |          |
| $d$, Cauchy $A$, $B$, $k$, $C$, $dzA$ (anisotropy) | 6    | 4.9 ± 0.2 | 263.7 ± 0.5 | 1.6211 ± 0.0004 | 0.0079 ± 0.0002 | -0.0122 ± 0.0004 |          |
| $d$, Cauchy $A$, $B$, $C$, $k$, grading | 6    | 8.0 ± 0.2 | 264.1 ± 0.4 | 1.6162 ± 0.0012 | 0.0100 ± 0.0001 | 4.0 ± 0.9 |          |

**Thermal annealing**

In Figure S1 the change in the refractive indices and the thickness is shown as function of the complete annealing treatment. Upon heating, the decrease in thickness caused by the removal of the spin-coating solvent competes with the thermal expansion caused by the increase in
temperature as is shown in Figure S1A. After an isothermal timestep of 1 hour at 250 °C, all residual solvent was removed and thermal expansion upon heating to 350 °C was observed (Figure S1C). At the same time, as 350 °C is above the glass transition of matrimid, the anisotropy decreased. A small but continuous decrease in thickness (~1 nm) and no significant changes occurred in the refractive index during the isothermal stage at 350 °C. The small change in thickness and negligible change in refractive index during this isothermal stage indicate that any possible structural changes that occur, such as cross-linking or crystallization, are of a very small degree. During a slow cooling to 25 °C (Figure S1E), a glass transition temperature was observed at ~309 °C and the anisotropy within the sample again increased.

![Graphs showing temperature, refractive index, and thickness changes](image)

**Figure S1.** The thickness (right axis), ordinary refractive index ($n_o$ at 632.8 nm) and extraordinary refractive index ($n_e$ at 632.8 nm) (left axis) as function of the annealing temperature and time. Upon heating to 250 °C (A) followed by an isothermal stage at 250 °C (B), residual solvent was evaporated. Upon further increase in temperature, anisotropy in the sample was being removed and thermal expansion was observed (C). During the 6 hours isothermal stage (D), a slight decrease
in thickness (~1 nm) and no changes in the refractive indices were observed. During a slow cooling from 350 °C to 25 °C (E), a glass transition temperature was observed at 309 °C and anisotropy was increased.

**Penetrant induced swelling**

For the *in situ* swelling measurements, to avoid over parameterization, a wavelength range of 450 nm to 900 nm was used. This allowed for removal of eliminating the absorption, $k$, which is strongly correlated with the thickness. For swelling measurements with toluene, an additional gradient was considered, as shown in Figure S2. By applying a gradient within the conventional optical model as described in Table S1, the optical model was able to describe the swelling of the matrimid within the first 2-3 hours more accurately. This can be explained by the fact that the solvent is penetrating as a front through the matrimid film, allowing part of the film to be swollen, but not the entire bulk. After 2-3 hours, the penetrant has penetrated throughout the bulk of the film, removing the thickness inhomogeneity. As result, the results of the optical model with gradient is similar as the optical model without gradient (fit parameters: $d, A, B, C, k, dzA$) after 2-3 hours.
**Figure S2.** Swelling degree (*SD*) and mean squared error (*MSE*) as function of time, as a result of a simple/normal optical model (left) and the application of a gradient in the optical model (Fit parameters: $d, A, B, C, k, dzA +$ grading) (right).

The calibration of the window offsets during the liquid swelling measurements was performed using a 60 nm SiO$_2$ calibration wafer which was measured *ex situ, in situ* dry and *in situ* with the liquid penetrant. The optical constants of $n$-hexane and toluene were determined with a digital multiple wavelength refractometer (Schmidt Haensch ATR-L) at 20°C for 7 different wavelengths (365.0 nm, 400.0 nm, 450.0 nm, 500.0 nm, 590.0 nm, 700.0 nm, 800.0 nm). A Cauchy dispersion relation was fitted to the obtained data to determine the refractive index at 632.8 nm. The fixed optical parameters used for the optical modelling in the liquid penetrants are shown in Table S2.

**Table S2.** The optical constants as used for toluene and $n$-hexane in the optical model at 20°C.

| Penetrant   | $n$ at 632.8 nm ± 0.001 | $A$   | $B$   | $C$   | Window offset |
|-------------|------------------------|-------|-------|-------|--------------|
| Toluene     | 1.494                  | 1.476 | 0.007 | 0.0003| -0.825       |
| $n$-hexane  | 1.374                  | 1.367 | 0.003 | -     | 1.431        |

**DRIFT-FTIR TEMPERATURE DEPENDENCE**

The DRIFT-FTIR absorbance spectra for each characteristic IR vibration of matrimid before, during and after annealing treatment are shown in Figure S3.
Figure S3. Temperature dependent DRIFT-FTIR absorbance spectra of matrimid during the annealing of a freshly spin-coated film at 25°C to 350 °C. Black line: 25°C, Blue: 55 min at 250 °C, Orange: 5 min at 350 °C, Dark red: 5 hours and 55 min at 350 °C, dashed blue: 250 °C upon cooling, dashed black: 25 °C after the heat treatment.

In Figure S4, the FTIR temperature dependence of an annealed ~3 µm matrimid film is shown. The C-N-C axial stretch and the C=C aromatic stretching are strongly influenced by the temperature and show a decrease in wavenumbers. This indicates a lower amount of energy is required to vibrate these specific groups. The effect is reversible, as with decreasing temperatures, the original wavenumbers were obtained again.
Figure S4. Temperature dependent IR spectra of ~3 µm matrimid film. Strong shifts to the lower energies were observed for the C-N-C axial stretch and the C=C aromatic stretching. The dashed black line indicates the FTIR spectrum at 25°C after the heat treatment. Resolution is 2 cm\(^{-1}\)

REPRODUCIBILITY OF BDS MEASUREMENTS

In Figure S5, the BDS result of toluene induced swelling in the second matrimid film is shown. As also shown in Figure 6 in the main manuscript, toluene consistently speeds up the \(\beta_2\)-relaxation, while the \(\beta_1\)-relaxation remains unchanged.
Figure S5. Reproducibility of ε” (A) and ε’ (B) for a ~260 nm dry matrimid film (closed black squares), exposed to toluene for 1 hour (blue open circles), 24 hours (orange open circles) and after drying with a continuous nitrogen flow after toluene exposure (open square). (C) The relaxation times of the two β-relaxations were determined for each frequency sweep time step and shown as function of exposure time. The grey margin above the symbols represent the standard error of the fit (for visualization purposes in positive direction only). For both samples, no changes in the β₁-relaxation was detected, and the β₂-relaxation shifts to the higher frequencies.
In Figure S6, the BDS result for the second sample of n-hexane induced swelling in a matrimid film is shown. N-Hexane influences the relaxation dynamics of both β-relaxations but no consistent change was observed when considering the results of both matrimid samples (Figure 7 in main manuscript and Figure S6).

Figure S6. Reproducibility of ε’’ (A) and ε’ (B) for a ~260 nm dry matrimid film (closed black squares), exposed to n-hexane for 1 hour (blue open circles), 16.5 hours (orange open circles) and after drying with a continuous nitrogen flow after n-hexane exposure (open square). (C) The relaxation times of the two β-relaxations were determined for each frequency sweep time step and shown as function of exposure time. The grey margin above the symbols represents the positive standard error of the fit (for visualization purposes in positive direction only). Both β-relaxations interact with the n-hexane, but the effect is not consistent.
DRIFT-FTIR PENETRANT INDUCED ABSORBANCE SPECTRA

For both \( n \)-hexane and toluene *in situ* DRIFT-FTIR measurements, a reference measurement was performed on a bare silicon wafer using the same measurement conditions. In Figure S7 (\( n \)-hexane) and Figure S8 (toluene), the IR absorbance spectra for different matrimid samples are shown. In these figures, the *in situ* was corrected for the absorbance of the penetrant by subtracting the reference signal of the pure penetrant on a bare silicon wafer.

![Spectra figures](image)

**Figure S7.** Corrected IR-absorbance spectra for 2 different matrimid samples exposed to \( n \)-hexane.

The dashed black line represents the reference measurement of a bare silicon wafer exposed to \( n \)-hexane. The black line is the original dry matrimid sample. The dashed red line represents the longest exposure time (i.e. 3 days for Hexane-2) and the red line represents 26 and 33 hours
exposure respectively for hexane-1 and hexane-2. All colors in between represent the different time steps (i.e. 1, 3, 6, 10, 16, and 21 hours).

**Figure S8.** Corrected IR-absorbance spectra for 2 different matrimid samples exposed to toluene. The dashed black line represents the reference measurement of a bare silicon wafer exposed to toluene. The black line is the original dry matrimid sample. The dashed red line represents the absorbance spectra after the addition of extra liquid toluene into the measurement cell (i.e. 3 hours after additional toluene was added) and the red line represents 26 and 27 hours exposure respectively for toluene-1 and toluene-2. All colors in between represent the different time steps (i.e. 1, 3, 6, 10, 16, and 21 hours).

Original data
In Figure S9 and Figure S10 the original absorbance spectra of matrimid for \( n \)-hexane and toluene exposure respectively are shown.

**Figure S9.** Original IR-absorbance spectra of 2 different matrimid samples exposed to \( n \)-hexane. The dashed black line represents the reference measurement of a bare silicon wafer exposed to \( n \)-hexane. The black line is the original dry matrimid sample. The dashed red line represents the longest exposure time (i.e. 3 days for hexane-2) and the red line represents 26 and 33 hours exposure respectively for hexane-1 and hexane-2. All colors in between represent the different time steps (i.e. 1, 3, 6, 10, 16, and 21 hours).
Figure S10. Original IR-absorbance spectra of 2 different matrimid samples exposed to toluene. The dashed black line represents the reference measurement of a bare silicon wafer exposed to toluene. The black line is the original dry matrimid sample. The dashed red line represents the absorbance spectra after the addition of extra liquid toluene into the measurement cell (i.e. 3 hours after additional toluene was added) and the red line represents 26 and 27 hours exposure respectively for toluene-1 and toluene-2. All colors in between represent the different time steps (i.e. 1, 3, 6, 10, 16, and 21 hours).