# Phase change dynamics in a polymer thin film upon femtosecond and picosecond laser irradiation

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## Abstract

The influence of the pulse duration on the laser-induced changes in a thin triazenepolymer film on a glass substrate has been investigated for single, near-infrared (800 nm) Ti:sapphire laser pulses with durations ranging from 130 fs up to 2.6 ps. Post-irradiation optical microscopy has been used to quantitatively determine the damage threshold fluence. The latter decreases from $\sim$800 mJ/cm$^2$ for a 2.6 ps laser pulse to $\sim$500 mJ/cm$^2$ for a pulse duration of 130 fs. In situ real-time reflectivity (RTR) measurements have been performed using a ps-resolution streak camera set-up to study the transformation dynamics upon excitation with single pulses of duration of 130 fs and fluences close to the damage threshold. Very different reflectivity transients have been observed above and below the damage threshold fluence. Above the damage threshold, an extremely complicated behaviour with oscillations of up to 100% in the transient reflectivity has been observed. Below the damage threshold, the transient reflectivity decreases by as much as 70% within 1 ns with a subsequent recovery to the initial level occurring on the ms timescale. No apparent damage could be detected by optical microscopy under these irradiation conditions. Furthermore, within the 395–410 mJ/cm$^2$ fluence range, the transient reflectivity increases by $\sim$10%. The analysis of these results indicates that the observed transformations are thermal in nature, in contrast to the known photochemical decomposition of this triazenepolymer under UV irradiation.
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*Keywords:* Laser irradiation; Phase change dynamics; Polymer

## 1. Introduction

Laser processing of polymers has been intensively studied for more than two decades now [1,2]. Most of the research has been concentrated on the study of the interaction mechanisms and applications of laser ablation, particularly upon UV irradiation, where many polymers of interest are highly absorbing. The role of the different ablation mechanism remains controversial, with both photothermal and photochemical processes being important [3]. One polymer group that is photochemically very active upon UV irradiation is that of the triazenepolymers [4] which feature superior ablation

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properties for irradiation at a wavelength of 308 nm [5].

In the present study, the behaviour of a triazene-polymer film has been studied upon irradiation with single ultrashort near-IR (800 nm) pulses, which due to their high intensities might be an alternative way of structuring by means of multi-photon absorption. The use of time-resolved optical measurements is a valuable tool for studying the transient fluence-dependent response of the irradiated material. In this study, time-resolved reflectivity measurements with sub-ns temporal resolution have been used for analysing the transformation dynamics while optical microscopy has been utilised for characterisation of the final state of the surface after irradiation. Both techniques provide complementary information regarding the physical processes induced by irradiation at this wavelength.

## 2. Experimental

The polymer film, with a chemical structure as shown in Fig. 1a, has been synthesised according to a procedure described elsewhere [6]. The samples for the experiments have been prepared on glass substrates by solvent casting or spin coating of a 10 wt.% solution of the polymer in a 1:1 mixture of cyclohexanone/chlorobenzene with one additional drop of a surfactant (Pluronic L-62), resulting in a final film thickness of $\sim 1$ μm.

A commercial chirped pulse amplification (CPA) Ti:sapphire laser system (Spectra Physics, Spitfire), providing linearly polarised pulses at a wavelength of 800 nm, was used for irradiation. By exploiting the CPA technique, the pulse duration has been continuously varied between 130 fs and 2.6 ps by changing the separation length of the diffraction grating and retro-reflector in the compressing section of the amplifier system. The duration of the laser pulses has been measured using a single-shot autocorrelator (Spectra Physics, SSA) by fitting the pulses to a temporal Gaussian profile. The polymer film is essentially transparent at the irradiation wavelength (photon energy $\sim 1.55$ eV) such that in the linear absorption regime, the optical penetration depth $1/\alpha$ exceeds the film thickness by several orders of magnitude.

In the irradiation set-up, the sample was placed at normal incidence close to the focal plane of a lens with 150 mm focal length, resulting in an almost circular laser spot on the surface, which corresponds, approximately to a spatial Gaussian distribution with a $(1/e^2)$ diameter of the order of 100 μm. An *xyz*-translation stage was used for precise positioning of the sample after each single pulse irradiation in air.

The temporal evolution of the surface reflectivity upon irradiation has been monitored using a single mode $Ar^+$ laser operating at 514.5 nm. This probe beam was focused at the centre of the fs/ps laser irradiated region to a spot diameter $(1/e^2)$ of $\sim 30$ μm, at an angle of incidence of $\sim 18°$. The intensity evolution of the reflected probe beam was then recorded by a streak camera (Hamamatsu Model C5680, equipped with a single sweep unit Model M5676; time-resolution of 350 ps in a time window of 50 ns) and by a photodiode/oscilloscope detection system (a few ns temporal resolution). Further details regarding this RTR set-up have been published elsewhere [7].

## 3. Results and discussion

Fig. 1b shows a series of optical micrographs of damage spots in the triazenepolymer film irradiated with a single laser pulse for different durations between 130 fs and 2.6 ps at fluence level of $720 \pm 20$ mJ/cm$^2$.

For a pulse duration of 130 fs, a damaged area with a diameter of $\sim 115$ μm has been formed (in the following we refer to *damage* if permanent material modification is visible by optical microscopy). Inside the ablated region, some irregularly re-deposited polymer filaments are observed. The diameter of the damaged area significantly decreases when the pulse duration is increased. Since a spatially Gaussian shaped laser beam has been used, this is indicative for an increasing damage threshold fluence. For the highest pulse duration of 2.6 ps, the applied fluence was not sufficient to induce damage of the polymer film.

A more detailed study of the damage threshold fluence as a function of the pulse duration has been performed according to a procedure suggested by Liu [8]. The laser pulse energy has been varied at a
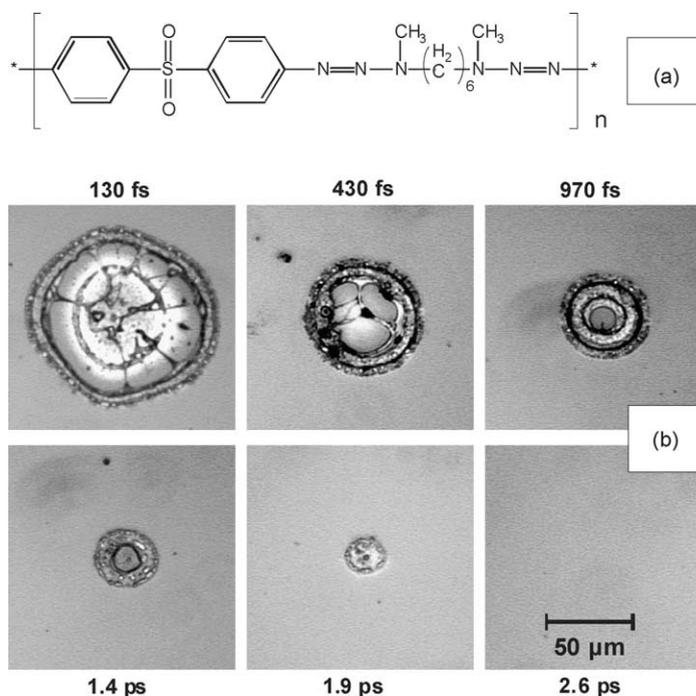
Fig. 1. (a) Chemical structure of the triazenepolymer and (b) optical transmission micrographs of damage spots in the triazenepolymer film irradiated with single laser pulses of different durations (130 fs to 2.6 ps) at a constant fluence of $720 \pm 20$ mJ/cm$^2$.

constant pulse duration, resulting in damage spots of different diameters. For a Gaussian shaped beam, the threshold fluence $\phi_{th}$ can be determined from a semilogarithmic plot of the squared outer damage diameter $D^2$ versus the incident maximum laser fluence $\phi_0$ via back-extrapolation of $D^2 \rightarrow 0$. Fig. 2
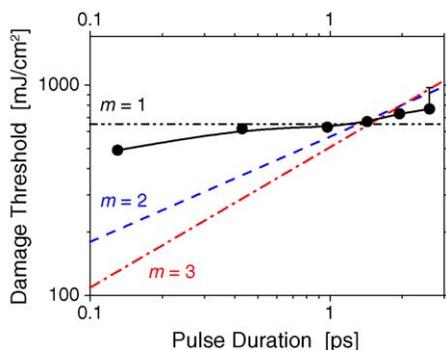


Fig. 2. Damage threshold fluence as a function of the pump pulse duration (circles with the solid line to guide the eye). The dashed and dotted lines represent least squares fits to the model of Stuart et al. [13] for the absorption of $m$ photons ($m = 1$–$3$).

shows the measured damage threshold fluence determined for several pulse durations between 130 fs and 2.6 ps in a double-logarithmic plot (circles).

The damage threshold fluence changes only between 495 mJ/cm$^2$ (for $\tau \sim 130$ fs) and $\sim 800$ mJ/cm$^2$ (for $\tau \sim 2.6$ ps) when the pulse duration is increased by more than one order of magnitude. The value of $\phi_{th}$ at 130 fs ($\sim 495$ mJ/cm$^2$) is more than a factor of two smaller than the damage thresholds typically observed under similar experimental conditions (800 nm, $\sim 130$ fs) for commercial bulk polymers (PI: 1000 mJ/cm$^2$ [9], PC: 1700 mJ/cm$^2$ [10], PMMA: 2600 mJ/cm$^2$ [10]). As pointed out by Jasapara et al., a thin dielectric film on a transparent substrate exhibits different optical properties (surface reflectivity, intensity distribution within the film) than the bulk material [11]. This will affect the damage threshold value. Our experimentally determined threshold values are also significantly higher than those observed for nanosecond UV irradiation at 308 nm, where threshold values around 25 and 60 mJ/cm$^2$ were respectively observed for a triazenopolymer

film and a commercial polymer, i.e. polyimide, with a similar absorption coefficient at that wavelength [12].

It is therefore clear that the mechanisms for laser-induced damage are different upon UV ns irradiation and near-IR femtosecond/picosecond irradiation (fs/ps irradiation). According to the generally accepted theory of laser induced breakdown in transparent dielectrics, damage is induced when a critical electron concentration in the conduction band of the order of $10^{21}$ cm$^{-3}$ is exceeded upon the laser irradiation [13]. Carrier generation due to both *nonlinear effects* (*m*-photon absorption, MPA) and *free-carrier absorption* (FCA) with subsequent *avalanche-ionisation* (AI) have to be considered [13] due to the high intensities of ultrashort laser pulses. Following the analysis of Stuart et al., the dependence of the damage threshold fluence on the pulse duration provides valuable information regarding the characteristic damage mechanism [13]. Neglecting the energy redistribution due to recombination and carrier diffusion during the laser pulse, the characteristic scaling law for a pure *m*-photon absorption induced damage process is found to be $\phi_{th} \sim \tau^{(m-1)/m}$. Hence, linear absorption processes ($m = 1$) such as the (small signal) interband absorption or free-carrier absorption show no dependence on the pulse duration. In contrast, the *m*-photon absorption scales with a power law. Fig. 2 also includes the best fit of the corresponding power laws for $m = 1$–3 to the experimental data. None of these curves show a satisfying agreement with the experimental data. Nevertheless, from the measured weak dependence of the damage threshold on the pulse duration, we conclude that the linear process of FCA with subsequent AI is the dominant damage mechanism and that there is only a small contribution due to MPA. Intrinsic defects, that are expected to pile up in the film close to the polymer/substrate interface, can also contribute to the AI process and would lead to a scenario in which the laser-induced damage is initiated at the polymer/substrate interface. Wherever damage is initiated, it most likely involves the breaking of the weakest bond of the triazenepolymer chain, which is an N–N bond (see Fig. 1a) with a bond strength of ∼3 eV. This bond cannot be directly broken by the absorption of a single 800 nm photon but it can be destroyed via impact ionisation through the (indirect) mechanism of FCA with subsequent AI.
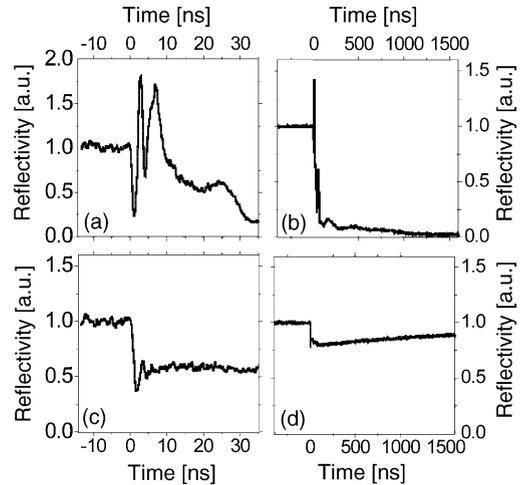


Fig. 3. Normalised reflectivity of the polymer film on glass after irradiation with single 130 fs laser pulse at a fluence above ((a and b) ∼495 mJ/cm$^2$) and below ((c and d) ∼490 mJ/cm$^2$) the ablation threshold as measured with the streak camera (a and c) and with the photodiode (b and d) on a longer timescale. Note the different scale of the reflectivity axis in (a).

RTR measurements have been performed for fluences around the damage threshold for pulse duration of 130 fs. Fig. 3 shows typical surface reflectivity transients induced for fluences slightly above (Fig. 3a and b) and below (Fig. 3c and d) the well defined threshold. In this figure, the surface reflectivity has been normalised to the initial value before the arrival of the ultrashort laser pulse. The reflectivity transients recorded by the streak camera during the first 35 ns are displayed in Fig. 3a and c, while Fig. 3b and d show the simultaneous measurements performed with the photodiode on a timescale up to 1.6 μs after irradiation.

At a fluence slightly above the damage threshold, the reflectivity shows a sharp drop, followed by rapid oscillations with a normalised amplitude around 0.75 lasting for a few nanoseconds (Fig. 3a). This behaviour is consistent with the formation of gas bubbles inside the film due to the decomposition of the polymer into gaseous components. Optical simulations of a thin polymer film on a glass substrate show that a decrease of the film refractive index *n* would cause a decrease of its reflectivity. The initial reflectivity drop in Fig. 3a can thus be related to a decrease of effective refractive index caused by the formation of gas in the polymer matrix. The

oscillations would then arise from interference effects at the gas/polymer interfaces as the bubbles expand. Dijkkamp et al. have already shown that gas bubbles can be formed at the polymer/substrate interface upon laser irradiation of non-absorbing polymer films on absorbing substrates [14]. The observed damage is thus most likely related with the decomposition of the film leading to its ablation. Note that the border regions around a damaged area (Fig. 1) can be affected by the formation of a rim, caused by material transport [3], recoil pressure [3] or changes in specific volume of the polymer [10].

When the laser fluence is decreased to just below the ablation threshold, large transient changes of the surface reflectivity are also observed which lead to a rapid decrease of the normalised reflectivity by more than 0.50 within the first ns (Fig. 3c). This decrease is followed by a second minimum after ∼100 ns (Fig. 3d) and a recovery towards the initial reflectivity on a ms timescale (not shown). Note that these transient reflectivity changes upon fs laser irradiation are significantly greater than those observed during quasi-static thermal heating measurements (heating rate of 1 °C/min) where the maximum reflectivity decrease is ∼11%.

In order to investigate these reflectivity changes for fluences below the ablation threshold in more detail, a systematic variation of the laser fluence has been performed for 130 fs laser pulses. Fig. 4 shows typical transients for three different fluences of ∼390 mJ/cm$^2$ (curve A: ≈0.79 × $\phi_{th}$), ∼400 mJ/cm$^2$ (curve B: ≈0.81 × $\phi_{th}$) and ∼490 mJ/cm$^2$ (curve C: ≈0.98 × $\phi_{th}$) as measured by the (a) streak camera and (b) photodiode detection system.

A rapid reflectivity decrease followed by a damped oscillation on the ns timescale is evident in the curves A and C (Fig. 4a), whereas curve B surprisingly shows a small transient reflectivity increase of ∼0.10. The reflectivity of the first peak ($R_{1st\ peak}$), either maximum or minimum, in the reflectivity transients is obviously fluence dependent. On a longer time scale up to ∼1.6 µs, the reflectivity transients show additional features (Fig. 4b). After the initial sharp dip (oscillation) the reflectivity in curve A undergoes a monotonous decrease to normalised values around 0.90 after 1.6 µs, whereas, in curve C, a characteristic minimum with a normalised reflectivity ($R_{min}$) below 0.80 has been observed after ∼100 ns, before
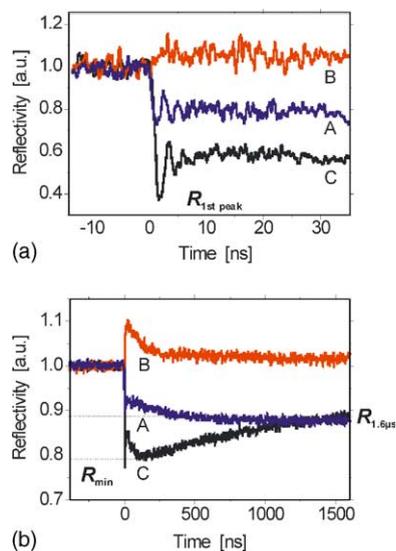


Fig. 4. Normalised reflectivity of the polymer film on glass after irradiation with a single 130 fs laser pulse at a three different fluences below the ablation threshold (curve A: ∼390 mJ/cm$^2$ ≈ 0.79 × $\phi_{th}$, curve B: ∼400 mJ/cm$^2$ ≈ 0.81 × $\phi_{th}$, curve C: ∼490 mJ/cm$^2$ ≈ 0.98 × $\phi_{th}$) as measured with the (a) streak camera and (b) photodiode.

recovering to 0.90 after 1.6 µs. The reflectivity in curve B always remains above that of the initial value while slowly decreasing in magnitude.

The characteristic parameters of the reflectivity transients, as shown in Fig. 4a and b, have been evaluated systematically in Fig. 5 which compiles the reflectivity of the first peak, either maximum or minimum ((a) $R_{1st\ peak}$, as measured by the streak camera), as well as the reflectivity of the later minimum ((b) $R_{min}$) and the reflectivity approximately 1.6 µs after the arrival of the fs laser pulse to the surface ((c) $R_{1.6\ µs}$) as a function of the laser fluence (the two latter parameters were determined from the photodiode transients). From these plots, three different fluence regimes (labelled I–III) can be distinguished below the ablation threshold.

These different fluence regimes are related to different processes in the polymer, which in turn may be related to the sample preparation, the material characteristics and alterations of its optical properties. The polymer has a glass transition temperature $T_g = 383$ K and a decomposition temperature $T_d = 567$ K (start of weight loss at 486 K). Assuming that the polymer decomposition starts at the weakest

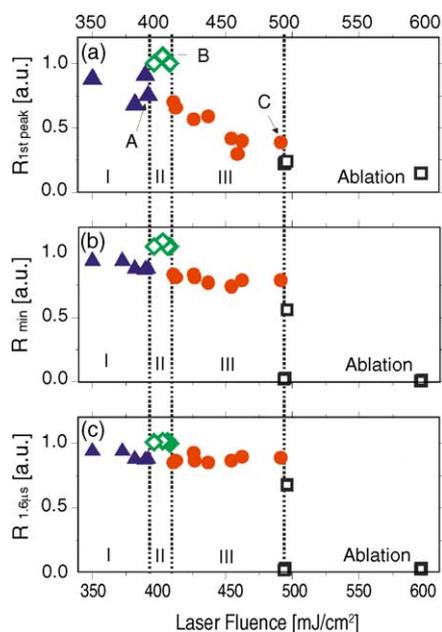Fig. 5. Normalised reflectivity of the first peak ((a) $R_{1st\ peak}$, streak camera), the minimum ((b) $R_{min}$, photodiode) and value after 1.6 µs, and ((c) $R_{1.6\ µs}$, photodiode) as a function of the laser fluence. The characteristic fluence regimes are separated by vertical dashed lines and labelled by different symbols (I–III and ablation). The data points corresponding to the curves displayed in Fig. 4 are marked by labels A–C.

N–N bond, gaseous $N_2$ will be created as the primary decomposition product. At a sufficiently high decomposition rate, these molecules will form bubbles inside the polymer matrix, thus leading to an increased pressure and probably also causing a surface expansion (in addition to thermal expansion and a change of the specific volume upon polymer chain fracturing). Another important aspect to consider is the fact that it is nearly impossible to completely remove the solvent from a polymer film prepared from a solution. For instance, it has been reported for PMMA that up to 20 wt.% of the solvent (chlorobenzene) remains in the polymer film [15]. This remaining solvent will most probably show a phase transition (liquid–gaseous) around 400–425 K upon heating, which will also result in the creation of gas bubbles in the polymer and the expansion of the surface. Both effects will result in a reduced effective refractive index.

Based on these considerations, it is possible to describe the three fluence regimes below the ablation threshold in terms of the tentative picture that follows:

*Regime I*: For fluences between ~350 and 395 mJ/cm$^2$ (full triangles), the characteristic reflectivity parameters ($R_{1st\ peak}$, $R_{min}$, $R_{1.6\ µs}$) decrease linearly with the laser fluence. We attribute this to the formation of gas bubbles mainly due to the boiling of the residual solvent which will lower the refractive index and, therefore, also the reflectivity. Since this occurs at temperatures above the glass transition temperature, these bubbles can diffuse out of the optically probed volume on the ms timescale thus explaining the subsequent long-term recovery of the reflectivity.

*Regime II*: Only in this very narrow fluence range between 395 and 410 mJ/cm$^2$ (open diamonds) does the reflectivity show an initial increase in both the streak camera ($R_{1st\ peak}$) and photodiode ($R_{min}$, $R_{1.6\ µs}$) transients. This might arise from the spatially modulated energy deposition expected upon pulse irradiation due to the formation of a standing optical wave inside the polymer film [11] with a periodicity of $\lambda/(2n)$. In this fluence regime, a decomposition of the polymer into gaseous $N_2$ is initiated only at the local maxima of this energy distribution. Due to the threshold behaviour of the decomposition, a spatially modulated refractive index profile is suddenly generated. This refractive index profile can act as a mirror-like dielectric multi-layer system, such that constructive interference effects increase the transient reflectivity when compared to the non-irradiated film. It is possible that a similar effect was not observed in regime I because the amount of solvent is too small to cause a significant reflectivity increase upon its boiling.

*Regime III*: Laser fluences between 410 and 495 mJ/cm$^2$ (full circles) induce transients which are similar to those observed in regime I. All three reflectivity parameters continue the linear fluence dependence as observed in regime I. In this regime III, the threshold for polymer decomposition is exceeded in the entire film such that the regions of decomposition, still separated in regime II, have now merged together. Hence, interference effects are no longer seen and the increasing gas content further reduces the reflectivity.

The transient behaviour of the polymer film upon irradiation with longer laser pulses of ps duration is essentially the same as in the case of 130 fs duration laser pulses: the three different regimes below the ablation threshold are again observed although at

Table 1
Fluence regimes observed for the irradiation of a triazenepolymer film on glass with different pulse durations of 130 fs and 1.9 ps

| Regime | Fluence | |
| --- | --- | --- |
| | 130 fs pulses (mJ/cm$^2$) | 1.9 ps pulses (mJ/cm$^2$) |
| I | <395 | <595 |
| II | 395–410 | 595–645 |
| III | 410–495 | 645–730 |
| Ablation | >495 | >730 |

correspondingly higher fluences. Table 1 summarises the fluence regimes observed for irradiation with fs laser pulses (130 fs) and compares it to the corresponding ranges observed for a pulse duration of 1.9 ps. The similarity of the fluence ratios between each regime suggests that the mechanisms responsible are similar for the different pulse durations even if higher fluence values are required for observing the material modifications upon irradiation with ps laser pulses [$\phi_{th}(1.9 \text{ ps}) \sim 1.5 \times \phi_{th}(130 \text{ fs})$].

## 4. Conclusions

Phase changes in triazenepolymer films on glass substrates upon irradiation with Ti:sapphire laser pulses with durations between 130 fs and 2.6 ps have been investigated by means of optical microscopy and real-time reflectivity measurements using a streak camera set-up (time window 50 ns) and a photodiode detection system (time window 2 μs). The complementary results reveal that ablation of the polymer film is dominated by free-carrier absorption with subsequent avalanche ionisation within the material which initiates the decomposition into gaseous products. Even below the ablation threshold, transient reflectivity changes of up to 70% of the initial reflectivity value were observed on a ns timescale followed by a slow recovery on a ms timescale. These sub-ablational reflectivity changes may be attributed to a glass transition in the polymeric material, which is proceeded by the gaseous decomposition of the remaining solvent and the polymer as well as by optical interference effects.

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