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Vapor-deposited organic glasses exhibit enhanced stability against photodegradation

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Photochemically stable solids are in demand for applications in organic electronics. Previous work has established the importance of the molecular packing environment by demonstrating that different crystal polymorphs of the same compound react at different rates when illuminated. Here we show, for the first time, that different amorphous packing arrangements of the same compound photodegrade at different rates. For these experiments, we utilize the ability of physical vapor deposition to prepare glasses with an unprecedented range of densities and kinetic stabilities. Indomethacin, a pharmaceutical molecule that can undergo photodecarboxylation when irradiated by UV light, is studied as a model system. Photodegradation is assessed through light-induced changes in the mass of glassy thin films due to the loss of CO₂, as measured by a quartz crystal microbalance (QCM). Glasses prepared by physical vapor deposition degraded more slowly under UV illumination than did the liquid-cooled glass, with the difference as large as a factor of 2. Resistance to photodegradation correlated with glass density, with the vapor-deposited glasses being up to 1.3% more dense than the liquid-cooled glass. High density glasses apparently limit the local structural changes required for photodegradation.

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1. Introduction

Organic glasses are amorphous materials widely used in modern technologies, including polymeric materials,^{1,2} pharmaceuticals,^{3,4} and organic electronics.⁵ For example, active layers in organic light emitting diodes (OLEDs) are vapor-deposited organic semiconductors in the glassy state. Compared to crystals, glassy layers are smoother and, since there are no grain boundaries, more homogeneous at the macroscopic level; both of these properties are critical for OLEDs. Organic molecules will be unavoidably degraded after prolonged illumination with light of sufficiently short wavelength,^{6,7} and photostability is a concern for both crystalline and amorphous organic solids. For example, photodegradation can cause the failure of organic electronics in both display^{8,9} and light harvesting technologies,¹⁰ and this is sometimes a more limiting factor than device efficiency.

Recently, physical vapor deposition (PVD) has been used to prepare organic glasses with exceptional properties that are not accessible by any other preparation method.¹¹ By properly controlling processing conditions such as substrate temperature and deposition rate, vapor deposition can form stable glasses that have higher density,^{11–15} enhanced kinetic stability,^{12,14–16} and lower enthalpy^{11,12,17–19} relative to the liquid-cooled glass. It has been estimated that thousands of years of slow cooling or physical aging would be required to achieve the same density

when starting from the liquid state.^{14–16,20} The most stable glasses prepared by PVD are much deeper in the potential energy landscape than liquid-cooled glasses.¹⁸ All of the exceptional properties of vapor-deposited glasses point to the activation barriers for molecular rearrangements in these materials being significantly higher than for liquid-cooled glasses.¹¹ Therefore, even though there is no precedent for modulation of photodegradation by controlling glass packing, PVD glasses are good candidates for investigation. This is particularly relevant since PVD is already used to prepare organic electronic devices such as OLEDs.

Previous work has established the importance of the solid-state molecular packing environment in controlling photodegradation by demonstrating that different crystal polymorphs of the same compound react at different rates when illuminated. We present two examples from the pharmaceutical field where photodegradation is an important concern. For carbamazepine, it has been established that UV irradiation results in the formation of carbamazepine cyclobutane dimer and carbamazepine 10,11-epoxide. For the three crystal polymorphs of carbamazepine, the rates of photodegradation vary by as much as a factor of 5.²¹ As another example, one of the three polymorphs of furosemide photodarkens at a rate six times smaller than the other polymorphs as a result of UV irradiation, indicating that some feature of the local packing provides stronger resistance to photolytic degradation.²² Given that crystals can efficiently modulate photodegradation by as much as a factor of 5, vapor-deposited glasses might also be able to

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have an impact given their increased density relative to the liquid-cooled glass.

Recent work has shown that molecular packing in amorphous organic solids can modulate the rate of some photo-induced processes. Physical vapor deposition (PVD) was used to prepare glasses of Disperse Orange 37, an azobenzene derivative, with a significant range of densities. Photoisomerization of Disperse Orange 37 was found to slow down by a factor of 50 in the most dense glass relative to the least dense glass, which was prepared by cooling the supercooled liquid.²³ In earlier work, Royal and Torkelson reported that photoisomerization of an azobenzene dispersed into a polymer glass can be slowed slightly (about 5%) as a result of physical aging for a few days.²⁴ Ref. 23 and 24 provide important precedents indicating that glasses with efficient packing can inhibit at least some photo-induced processes. At present, there are no reports on whether efficient glass packing can slow photodegradation.

In this work, we test whether efficient molecular packing in amorphous organic solids leads to resistance against photodegradation. Here we utilized photodegradation of vapor-deposited indomethacin as a model system. It is known that indomethacin can undergo photodecarboxylation when irradiated by UV light (Scheme 1).²⁵ In addition, indomethacin has been found to form high-density glasses by vapor-deposition, with the density increase as much as 1.3% relative to the liquid-cooled glass.¹⁶ In this work, we vapor-deposited indomethacin onto substrates held at different temperatures to obtain glasses with different initial densities. We used a quartz crystal microbalance (QCM) to compare the mass loss induced in the different indomethacin glasses during UV light irradiation as a result of photodecarboxylation. Experiments were also performed on liquid-cooled glasses, including aged samples.

We find that photodegradation of vapor-deposited indomethacin can be significantly modulated by substrate temperature during deposition. The optimum vapor-deposited glass, prepared at about $0.85T_g$, photodegrades as much as two times more slowly than the liquid-cooled glass, depending upon the temperature at which the sample is irradiated. This is the first demonstration that glass packing can modulate photodegradation. We observe a good correlation between decreased photodegradation and increased glass density of vapor-deposited glasses. For indomethacin, vapor-deposited glasses can be more resistant to photodegradation than liquid-cooled glasses, and enhanced photostability might be a general phenomenon for dense glasses prepared by PVD. We discuss these new results on photodegradation together with previous results on photoisomerization. For the particular reactions studied, we propose

that local volume changes required by molecular rearrangement during photodegradation are much smaller than for those required for photoisomerization. For applications such as organic electronics, where photodegradation is an important cause of device failure,^{8,9} this work suggests a pathway to improve device lifetimes.

2. Experimental methods

2.1 Preparation of vapor-deposited indomethacin glasses

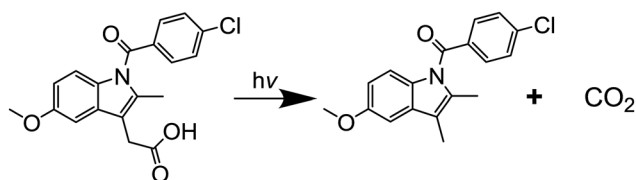
Glassy films of indomethacin were prepared by physical vapor deposition (PVD). Indomethacin (99% purity) was obtained from Sigma Aldrich and used as received. PVD was performed in a vacuum chamber with a base pressure of 10^{-7} Torr. Indomethacin was placed in a crucible that was resistively heated and the deposition rate was controlled by tuning the heater power. The deposition rate was monitored by a quartz crystal microbalance (QCM) and kept at a constant value of 2 \AA s^{-1} for all experiments reported here. For most of our experiments, the sample substrates were gold-coated quartz crystal resonators suitable for use in a QCM device as described below. During deposition, each quartz crystal resonator was in good thermal contact with a copper finger whose temperature was controlled at a constant value. For a few experiments that did not involve mass measurements, we utilized samples deposited onto a silicon wafer with a temperature-gradient imposed upon it; thus one sample contained a library of glasses prepared at many different substrate temperatures.¹⁶ In all cases, the thicknesses of the as-deposited PVD glasses were about 300 nm as measured by ellipsometry. Liquid-cooled glasses were prepared by vapor-deposition at a substrate temperature above T_g , followed by cooling to room temperature at 1 K min^{-1} . For indomethacin cooled at 1 K min^{-1} , $T_g = 310 \text{ K}$.

2.2 Kinetic stability and density measurements

The kinetic stabilities and densities of vapor-deposited indomethacin thin films were measured by spectroscopic ellipsometry (J. A. Woollam, M-2000). Ellipsometry is an optical technique that measures the thickness and refractive indices of thin films. Similar to our previous work,¹⁶ we utilized measurements at three incidence angles and used an anisotropic Cauchy model to fit all the ellipsometric data between 500 and 1000 nm. To measure kinetic stability and density, ellipsometry was performed on samples placed on a custom-built hot stage, and the temperature was increased at 1 K min^{-1} from room temperature to 335 K. Immediately after heating, the supercooled liquid was cooled at 1 K min^{-1} into the liquid-cooled glass and heated/cooled two more times at 1 K min^{-1} . Please note that we use the term “kinetic stability” to refer to the ability of a glass to resist rearrangement upon increasing temperature while “photostability” is used to describe resistance to degradation induced by UV illumination.

2.3 Photodegradation measurement

The light irradiation experiment used to test photodegradation of indomethacin glasses was performed in a quartz reactor



Scheme 1 Photodegradation of indomethacin under UV irradiation.

filled with nitrogen gas. A 312 nm UV lamp (Spectroline EBF-260C, 20 nm bandwidth) was used as the light source to induce the photodegradation reaction. The sample was illuminated at normal incidence with irradiance of $40 \mu\text{W cm}^{-2}$. For the ~ 300 nm thick films that we utilized, approximately 70% of the 312 nm light is absorbed in one pass through the film. During irradiation, a quartz microbalance (QCM) was placed in the quartz reactor at ambient pressure to continuously measure the mass decrease due to the loss of CO_2 that results from the reaction shown in Scheme 1. For irradiation below room temperature, the quartz reactor was cooled by dry ice and the temperature of QCM was controlled within 1°C variation during the photodegradation, as measured by a thermocouple in contact with the QCM. A 5 MHz AT-cut quartz plate (Inficon Inc.) with a polished gold electrode was used as the QCM resonator. QCM is widely used as a sensitive mass detector in many gas uptake measurements.^{26,27} For films in this thickness range, the frequency shift of the resonator can be related to the mass change of the sample by the Sauerbrey equation:²⁸

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q\mu_q}}\Delta m \quad (1)$$

In eqn (1), f_0 is the resonant frequency (Hz), Δf is the frequency change, Δm is the mass change, A is the piezoelectrically active crystal area, ρ_q is the density of quartz (2.648 g cm^{-3}), and μ_q is the shear modulus of quartz for the AT-cut crystal ($2.947 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-2}$). Since f_0 , A , ρ_q , and μ_q are all known, Δm can be calculated from Δf . In this way, we can monitor the photodegradation of the glassy thin films in real time. Below we present the fractional mass change; the initial mass is calculated using the ellipsometrically determined thickness of the film and the absolute density of amorphous indomethacin (1.32 g cm^{-3}).²⁹

3. Results

3.1 QCM measurement of photodegradation during irradiation

To demonstrate that QCM is an effective method to characterize the photodegradation of indomethacin, we first measured the mass loss of a liquid-cooled indomethacin glass during UV irradiation. The mass loss occurs as a result of photodecarboxylation (Scheme 1) with carbon dioxide gas escaping the film. In previously published work, the reaction product was identified by IR spectroscopy and liquid chromatography/mass spectrometry (LCMS).²⁵ As shown in Fig. 1, the mass of the liquid-cooled glass begins to decrease immediately upon irradiation, indicating continuous photodegradation. After nearly two days of irradiation, the mass approximately reaches steady-state. This is consistent with the view that all indomethacin molecules have reacted at this point. By fitting the experimental data with an exponential function, the overall mass loss is estimated to be about 12.5% at steady-state, which is reasonably consistent with the theoretical maximum mass loss 12.3% calculated from stoichiometry (Scheme 1). This provides confidence that we

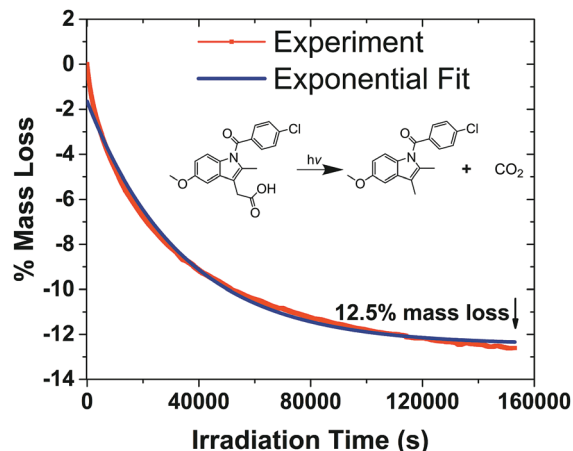


Fig. 1 Mass loss for a liquid-cooled glass of indomethacin as a function of UV irradiation time. Red symbols represent experimental results obtained with the quartz crystal microbalance and the blue curve is exponential fit.

understand the chemical transformation occurring in glassy indomethacin as a result of UV irradiation.

3.2 Determination of glass density

Spectroscopic ellipsometry was used to characterize the kinetic stability and density of PVD glasses of indomethacin. An example of this procedure is shown in Fig. 2. For this experiment, the indomethacin thin film was vapor-deposited at $T_{\text{substrate}} = 260 \text{ K}$ ($0.84T_g$) onto a polished gold QCM resonator. The procedure used here is the same as in previous reports except for the substrate material.^{15,16,30} Three different temperature ramping cycles were performed on each PVD glass. During the first temperature cycle, the as-deposited indomethacin was heated from 295 K to 335 K and then cooled back to 295 K. Two more heating and cooling cycles were also performed, and all heating and cooling rates were 1 K min^{-1} . During the initial heating, the thickness change below 325 K is due to the thermal

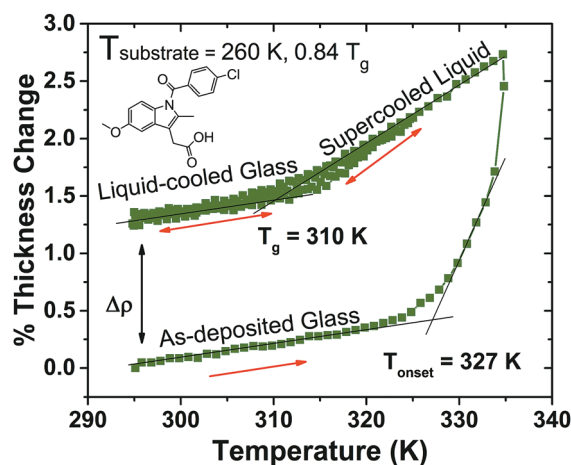


Fig. 2 Thickness changes for a vapor-deposited glass of indomethacin during temperature ramping at 1 K min^{-1} . The green symbols represent experimental data for a sample prepared at $T_{\text{substrate}} = 260 \text{ K}$ ($0.84T_g$). The sample thickness is about 300 nm.

expansion of the glassy solid. The as-deposited sample begins to transform into the super-cooled liquid at the onset temperature of 327 K. The onset temperature, which characterizes the kinetic stability of the as-deposited glass, was determined from the beginning of the transformation into the supercooled liquid. The subsequent cooling prepares the liquid-cooled glass, with the glass transition temperature $T_g = 310$ K. The second and third cooling runs in Fig. 2 closely reproduce the first cooling curve, as expected.

Fig. 2 illustrates that the glass vapor-deposited at $T_{\text{substrate}} = 260$ K exhibits a high onset temperature and high density, relative to the liquid-cooled glass. The onset temperature during the first heating is about 17 K higher than the T_g of the liquid-cooled glass, indicating increased kinetic stability. The density of as-deposited glass relative to the liquid-cooled glass was determined by the percentage thickness change as a result of the first heating/cooling cycle. In this case, the as-deposited glass is about 1.3% more dense, which is consistent with a previous report of vapor-deposited indomethacin.¹⁶ We also prepared and characterized samples at five substrate temperatures in addition to $0.84T_g$. Photodegradation experiments were performed on all these glasses and will be discussed in the next section.

3.3 Influence of PVD substrate temperature on photodegradation

Fig. 3 shows the comparison of the photoinduced mass loss for vapor-deposited and liquid-cooled glasses of indomethacin and reveals that the PVD glasses display slower photodegradation, *i.e.*, enhanced photostability. These tests followed a similar protocol as described in Section 3.1, with irradiation taking place at 295 K. Immediately after irradiation begins, the mass starts to decrease for all glasses. After 2000 s had elapsed, the liquid-cooled glass lost nearly 2.4% of its total mass, indicating that about 1/5 of the indomethacin had been decarboxylated. In contrast, PVD glasses photodegrade more slowly and the optimum sample ($T_{\text{substrate}} = 0.84T_g$) loses about 1.5% of its total

mass in 2000 s. By comparing the mass loss of the most stable vapor-deposited glass and the liquid-cooled glass, a decrease in the rate of photodegradation of about 40% can be observed.

Photodegradation of an aged liquid-cooled glass was also investigated and showed a very small change in the reaction rate relative to the freshly prepared liquid-cooled glass, as indicated by the grey curve in Fig. 3. The aged glass was prepared by cooling liquid indomethacin at 1 K min^{-1} and annealing at 277 K ($T_g - 33$ K) for a week. The aged glass was about 0.18% more dense than the freshly prepared liquid-cooled glass, as measured by ellipsometry. As shown in Fig. 3, the aged glass lost 2.2% of its mass as a result of 2000 s of irradiation.

A comparison of the rate of photodegradation for vapor-deposited and liquid-cooled glasses is summarized in Fig. 4. Fig. 4a shows the light-induced mass loss at the irradiation time of 2000 s. The liquid-cooled glass degrades about 1.5 times more than the optimum vapor-deposited glass, prepared at the substrate temperature of 260 K. Fig. 4b shows the densities of indomethacin glasses vapor-deposited at different substrate temperatures relative to the liquid-cooled glass.¹⁶ All the glasses investigated in this study that are deposited at $T_{\text{substrate}} < T_g$ show higher density than the liquid-cooled glass.

Comparing Fig. 4a and b, we see a strong correlation between decreased photodegradation and increased density. For this comparison, we utilize data from the early stages of the photoreaction to best characterize the dependence of photodegradation on the state of the glass. We verified that choosing a reaction time less than 2000 s would not change our conclusions about the relative stabilities of the different glasses. The photodegradation reaction changes the density and kinetic

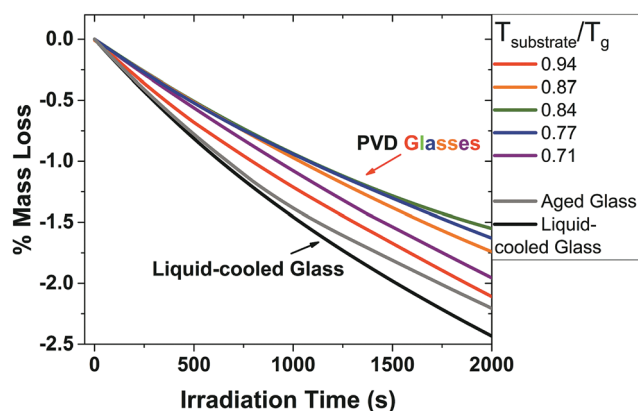


Fig. 3 Mass loss for vapor-deposited and liquid-cooled glasses of indomethacin as a function of irradiation time at 295 K. The black curve is liquid-cooled glass and the colored curves represent glasses vapor-deposited at the substrate temperatures indicated.

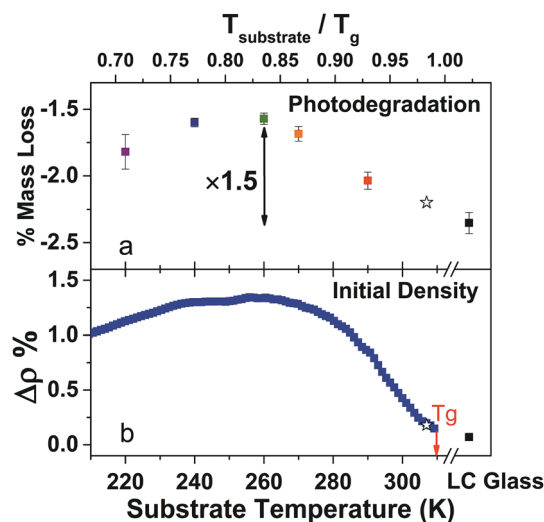


Fig. 4 Mass loss as a result of photodegradation and density of vapor-deposited glasses of indomethacin, as a function of substrate temperature during deposition, with comparison to the liquid-cooled (LC) glass (black solid square) and the aged glass (black open star). (a) Mass loss after 2000 s irradiation. (b) Density of as-deposited glasses relative to the liquid-cooled glass; filled symbols are data from ref. 16. A strong correlation is observed between resistance to photodegradation and density.

stability of the glass, as we discuss below, and so we did not investigate longer reaction times.

The two panels of Fig. 4 also include data on the aged liquid-cooled glass and this data supports the correlation between increased density and decreased photodegradation. These data points were placed in the figure as follows. The aged glass was plotted on the *x*-axis in Fig. 4b such that the aged glass density falls on the data points measured for the PVD glasses. This same *x*-axis position was then used in Fig. 4a to plot the mass loss observed for the aged sample.

3.4 Influence of irradiation temperature on photodegradation

The influence of irradiation temperature on photodegradation of indomethacin glasses was also investigated, and the stability of vapor-deposited glasses relative to the liquid-cooled glass was observed to increase at lower irradiation temperature. The solid lines in Fig. 5 show the mass loss of indomethacin glasses during irradiation at 279 K. (This is 16 K lower than the irradiation temperature used for Fig. 3 and 4.) As a result of 2000 s of irradiation, the liquid-cooled glass lost about 1.75% of its initial mass, while the optimum vapor-deposited glass, which was prepared at 260 K, lost about 0.91% of its initial mass. The glass vapor-deposited at 290 K shows an intermediate mass loss of 1.2%. For irradiation at 279 K, the mass loss of the liquid-cooled glass is about two times greater than that of the optimum vapor-deposited glass. For all glasses studied, photodegradation is less efficient at lower irradiation temperature, indicating that a thermal activation process is involved. Further discussion of the degradation mechanism is given below.

3.5 Properties of vapor-deposited glasses after photodegradation

Results presented above show that the packing of indomethacin molecules in the amorphous state can have a significant influence on the rate of photodegradation. Of course, rearrangements in the glass due to photodegradation would be expected to disrupt the packing. To gain some insight into the extent to which photodegradation alters the properties of indomethacin glasses,

we performed ellipsometry and X-ray scattering measurements on a few samples directly following 2000 s of irradiation.

We found that the photodegradation that occurred as a result of 2000 s of UV irradiation substantially diminished the density and kinetic stability of indomethacin glasses. For indomethacin vapor-deposited at 266 K ($0.86T_g$), as shown in Fig. 6, the onset temperature upon the first heating is 312 K, which is a much lower value than the 327 K value observed for similar samples that were not irradiated. Non-irradiated samples deposited at the same substrate temperature are 1.3% more dense than the liquid-cooled glass, while we only observed a 0.4% density change after transforming the photo-degraded glass. Both the onset temperature and density show that the efficient packing of the as-deposited glass was mostly destroyed after 2000 s of irradiation.

The influence of photodegradation on the average molecular orientation of the indomethacin molecules can be inferred from birefringence measurements before and after irradiation. Fig. 7 shows measurements of the birefringence of several indomethacin glasses as a function of irradiation time. As previously reported, the as-deposited glasses of indomethacin¹⁶ and several other organic molecules^{5,31,32} are birefringent, indicating anisotropic molecular orientation. The liquid-cooled glass has an initial birefringence of zero, which is consistent with random molecular orientation. During the irradiation, birefringence of vapor-deposited glasses is nearly constant, indicating that molecular orientation barely changed during photodecarboxylation. (In making this statement, we make the reasonable assumption that the polarizability tensors of indomethacin and its photoproduct are similar.)

We performed wide angle X-ray scattering measurements (not shown) on a few vapor-deposited glasses after photodegradation, and found that the anisotropic peak ($q = 0.57 \text{ \AA}^{-1}$) that has been interpreted³³ in terms of tendency towards molecular

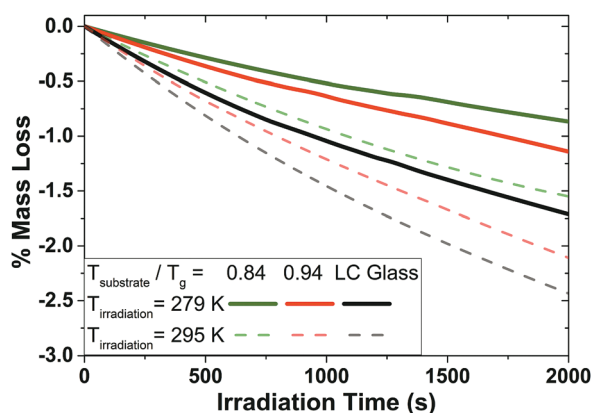


Fig. 5 Mass loss for vapor-deposited and liquid-cooled glasses of indomethacin as a function of irradiation time. Solid lines are results for irradiation at 279 K; dashed lines are results obtained at 295 K.

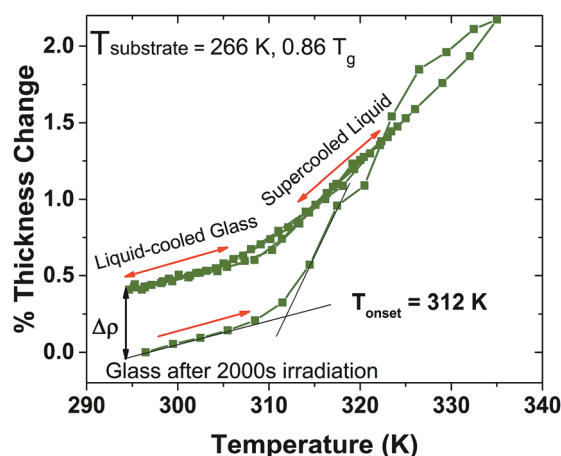


Fig. 6 Thickness changes for a vapor-deposited glass of indomethacin during temperature ramping (1 K min^{-1}) immediately following UV irradiation at 295 K. The green symbols represent experimental data for a sample prepared at $T_{\text{substrate}} = 266 \text{ K}$ ($0.86T_g$) and irradiated for 2000 s. Irradiation partially erases the initially high density of the vapor-deposited glass and eliminates the kinetic stability.

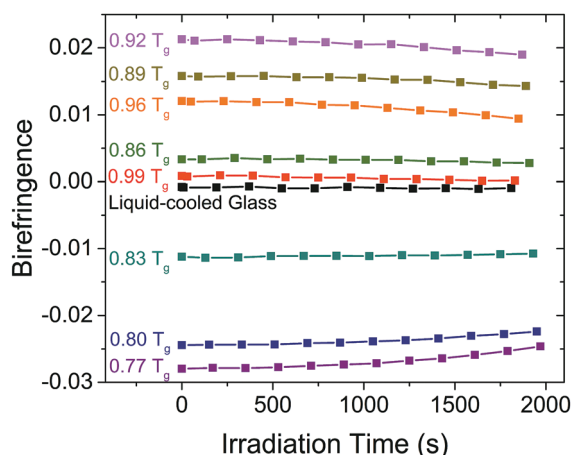


Fig. 7 Birefringence measurements for vapor-deposited and liquid-cooled glasses of indomethacin during UV irradiation at 295 K. The temperature of the substrate during deposition is indicated.

layering still exists after photodegradation. While Fig. 6 shows that photodegradation disrupts packing enough to eliminate the kinetic stability of the PVD glass, the birefringence and X-ray scattering show that large scale molecular rearrangements do not occur as a result of photodegradation.

4. Discussion

We have shown, for the first time, that photodegradation of organic molecules can be significantly modulated by packing in the amorphous state. More specifically, we have shown that PVD can prepare glasses of indomethacin that display enhanced stability against photodegradation. At the irradiation temperature of 279 K, the optimum vapor-deposited glass photodegrades more slowly than the liquid-cooled glass by a factor of 2. Previous work in organic crystals has shown that photodegradation can depend upon the crystal polymorph. For example, among the three polymorphic modifications of carbamazepine, polymorph I photodegrades 5.1 time more slowly than polymorphs II while polymorph III shows intermediate behavior.²¹ For crystal polymorphs, different photochemical reactivity has been attributed to the topochemistry principle that the reaction will involve nearest-neighbor molecules or functional groups and will occur with minimum atomic and molecular movement.^{34,35} In contrast, amorphous materials have a large number of local packing motifs and this approach does not seem appropriate. So why do glasses prepared by PVD, in common with crystals, show a prominent ability to modulate photochemistry?

The current work and literature precedents suggest that glass density plays a key role in modulating the rate of photo-induced changes in organic glasses. In the present work, this connection is shown by the strong correlation between photodegradation and glass density in Fig. 4a and b. The correlation that exists for vapor-deposited glasses also describes the behavior of liquid-cooled glasses and aged liquid-cooled glasses. Glass density also played an important role in our previous study of photoisomerization in glasses of Disperse Orange 37,

an azobenzene derivative.²³ We observed that photo-induced changes in the glass structure could be suppressed by a factor of 50 by preparing high density glasses with PVD and a strong correlation was observed between glass density and photo-induced structural changes. In that study,²³ molecular simulations demonstrated that molecular packing of higher density glasses can more effectively restrict molecules that start in the *trans* state from reaching the *cis* state after excitation. In another study of an azobenzene derivative tethered to a PMMA polymer in the glassy state, it was demonstrated that optically induced photoisomerization can be hindered by density increases caused by high pressure.³⁶ In a related set of experiments, the photostability of materials used in organic solar cells was tested in the presence of oxygen.³⁷ In that work, neat films of polymers, oligomers and small molecules, both in crystalline and amorphous states, were compared. Over the entire set of materials, a broad correlation was observed between density and photostability.

Having shown here that high-density glasses can inhibit photodegradation, we wish to speculate briefly about the mechanism of this process at the molecular level. Fig. 8 shows a generic energy diagram for photodegradation in the gas phase, as proposed by Nakashima and Yoshihara,³⁸ and provides background for our discussion. In this scenario, after indomethacin is photoexcited to the S₁ state from the ground state by a 312 nm photon, the molecule can access the repulsive potential R through a thermal excitation and dissociate such that a molecule of CO₂ is eventually formed. During this process, we imagine that the length of the C–C bond connecting the carbonyl carbon to the indole ring will be extended before it eventually breaks to release the fragment that will yield CO₂. Our results for the temperature dependence of photodegradation, as shown in Fig. 5, are consistent with the presence of a thermal activation step along the path to carbon dioxide formation. From this data, the activation energy for photodegradation of the liquid-cooled glass is estimated to be about 13 kJ mol^{−1} while 23 kJ mol^{−1} is obtained for the PVD glass that best resists photodegradation.

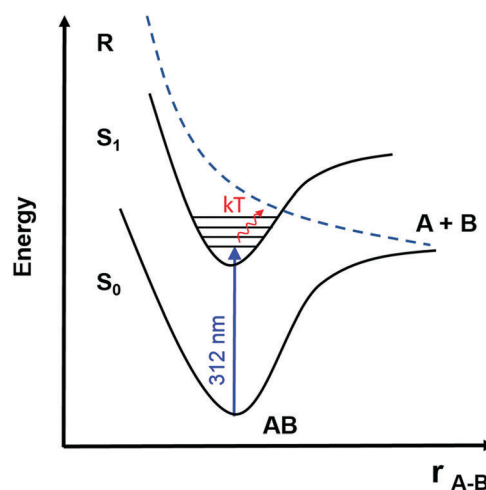


Fig. 8 Schematic energy diagram for photodegradation of indomethacin.

We do not imagine that the relative energies of the molecular states are altered significantly by the packing of the glass, so we interpret the larger activation energy of the PVD glass to indicate an increased barrier for the photolytic process that is imposed by the tight packing of the surrounding molecules. Perhaps the initial lengthening of the C–C bond with the indole ring is more difficult with more tightly packed neighboring molecules. A related interpretation has been given for the photoisomerization experiments of Disperse Orange 37. For that case, molecular dynamics computer simulations indicate that neighboring molecules in the high density glass more efficiently block the twisting motion required to access the *cis* state.²³ For amorphous materials generally, we speculate that the molecular rearrangements required to reach the product state are impeded to a greater extent in a higher density glass.

Although efficient glass packing can inhibit both photodegradation and photoisomerization in organic glasses, the photodegradation of indomethacin depends less sensitively on glass density than does the photoisomerization of Disperse Orange 37. During illumination at 295 K, a 1.3% increase in glass density decreases photoisomerization by a factor of 50 while this same density change slows photodegradation by only a factor of 1.5. We interpret this to mean that the *trans* to *cis* reaction for Disperse Orange 37 requires a greater rearrangement of the surrounding molecules than does the photodegradation of indomethacin. It is possible that the extent of the required rearrangement would be at least approximately captured by the activation volumes for these reactions. In high-pressure experiments on an azobenzene derivative similar to Disperse Orange 37,³⁶ the activation volume of photoisomerization was reported to be 111 Å³. We are unaware of any similar measurements for the photodegradation process of indomethacin but we expect that a considerably smaller activation volume would be obtained. It would be useful if the activation volumes for these two reactions could be obtained directly either from experiment or in a quantum calculation.

Although the experiments reported here show a strong correlation between high density and slow photodegradation in organic glasses, the reader should be cautious inferring causality. High density glasses prepared by PVD also have low enthalpy and high moduli.¹⁶ To a first approximation, these three properties change in a correlated manner as a function of substrate temperature during deposition. Thus, while high density might be responsible for slow photodegradation in indomethacin, the data presented here are equally consistent with the view that high moduli or low enthalpy is the cause. In order to distinguish among these possibilities, it would be useful to test photodegradation on high density glasses prepared by an alternative method, such as pressurizing a liquid-cooled glass.³⁹ Glasses prepared by pressure do not have the low enthalpy that characterizes PVD glasses.

5. Conclusion

We have shown that the photodegradation of an organic molecule can be significantly modulated by packing in the

amorphous state. The photodegradation of high-density glasses of indomethacin can be slowed down by as much as a factor of 2 relative to the liquid-cooled glass by selecting the correct substrate temperature for the vapor-deposition process. Suppression of photodegradation strongly correlates with glass density. The decreased photodegradation of high-density glasses was attributed to the constraint that the local packing exerts on the molecular rearrangement (bond extension and breaking) that happens in the PVD glasses as a result of irradiation.

We expect that the enhanced stability against photodegradation in well-packed glasses is a general effect for organic molecules and that this effect can be exploited in organic electronics. So far, PVD has been reported to prepare glasses with high density and high kinetic stability for more than thirty organic molecules, some of which are used in the active layers of OLEDs.¹³ We expect that those high-density glasses will result in higher energy barriers for photodegradation, which is a common mechanism for device failure. Moreover, as PVD is already used in industry to produce OLEDs, it would be of great interest if device lifetime could be increased by optimizing the preparation conditions to produce the most dense glass. Operational lifetime is considered to be a bottleneck to the further improvement of OLED display performance, especially for blue emitters.⁹ We note that the factor of 2 increase in stability against photodegradation for indomethacin was obtained for irradiation at $T_g - 31$ K (279 K). An even greater relative increase in stability would be expected at $T_g - 60$ K, which would be typical for many OLEDs molecules if illuminated at room temperature. Although we do not know whether a factor of 2 inhibition of photodegradation will be observed in other systems, our research provides a clear proposal for how to create more photostable glasses for organic electronics. Furthermore, the deposition conditions that optimize resistance to photodegradation also produce glasses with high thermal stability^{13,31} and low uptake of atmospheric gases.⁴⁰ It is likely that all of these features work to enhance the lifetime of devices built from organic glasses. Consistent with this view, Esaki and coworkers very recently reported that the electronic properties of films of organic semiconductors were more stable over time if vapor deposition conditions were optimized to prepare the highest density glasses.⁴¹

Conflicts of interest

There are no conflicts of interest to declare.

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