THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Letter

pubs.acs.org/JPCL

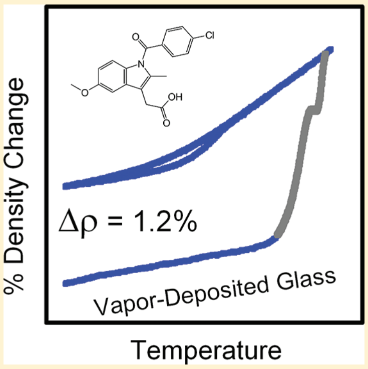
Molecular Orientation in Stable Glasses of Indomethacin

Shakeel S. Dalal and M. D. Ediger*

Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706, United States

S *Supporting Information*

ABSTRACT: Spectroscopic ellipsometry has been used to measure the properties of indomethacin prepared by physical vapor deposition at $T_{\mathrm{substrate}}/T_g$ = 0.78, 0.84, and 0.90. The as-deposited glasses exhibited high kinetic stability and had densities 0.8−1.2% higher than the ordinary glass prepared by cooling the liquid at 1 K/min. Deposition at the higher temperatures yielded glasses with positive birefringence (up to Δn = 0.028), while the lowest-temperature sample was negatively birefringent (Δn = −0.015). These results indicate that substrate temperature can be used to manipulate molecular orientation in high-density and high-stability glasses. The data for the supercooled liquid and the ordinary glass of indomethacin are reasonably consistent with the Lorentz−Lorenz equation, but significant deviations are noted with the as-deposited materials.



SECTION: Glasses, Colloids, Polymers, and Soft Matter

Glasses contain a large number of local packing arrangements. This allows their properties to be tuned continuously, by changes in composition or processing conditions, to an extent that is impossible to achieve with crystalline materials. For example, graded-index optical fibers have composition changes along the radial direction that optimize the refractive index profile. The large number of local packing arrangements also allows anisotropy to be introduced into glassy materials with continuous control. Oriented polystyrene glasses are utilized for their superior optical properties. The tempering of silicate glasses, either by chemical or thermal treatment, introduces anisotropic stresses that increase the modulus and alter fracture properties.[1] Organic glasses are utilized in organic light-emitting diodes (OLEDs), and the distribution of molecular orientations in these glasses is typically not random.[2,3] It has been argued that an anisotropic distribution of molecular orientations can increase OLED efficiency by increasing the charge mobility and directing emission away from the plane of the device.[3]

Unfortunately, the large number of local packing arrangements in a glass can also lead to instability in the form of slow structural relaxation or physical aging. A glass that is prepared by cooling a supercooled liquid (SCL) at a few degrees per minute will typically densify and become more rigid over the course of months and years.[4,5] This occurs as a result of molecular rearrangements that replace one local structure with one of the many other possible packing arrangements. Eventually, structural relaxation slows to a negligible rate, but waiting for this to occur is usually not feasible, and thus, kinetic instability limits the use of glassy materials in some applications.

Recent developments indicate that it may be possible to produce glassy materials that combine continuously tunable material properties with high kinetic stability. It has been shown that organic glasses with high kinetic stability can be prepared by physical vapor deposition.[6−8] Deposition onto substrates near 85% of the conventional glass transition temperature (T_g) can prepare materials that have many of the properties expected for glasses that have been aged for thousands or millions of years, including elevated density,[6,9] higher mechanical moduli,[10] and reduced uptake of atmospheric gases.[11]

It is important to investigate the extent to which average molecular orientation can be manipulated during glass preparation while maintaining high density and high kinetic stability in the resulting material. Yokoyama et al. established that physical vapor deposition can produce organic glasses with an anisotropic distribution of molecular orientations that can be controlled by varying the substrate temperature;[12] it is not known whether or not these glasses exhibit high density and high kinetic stability. Dawson et al. established that high-stability vapor-deposited glasses of indomethacin (IMC) and trisnaphthylbenzene isomers can show an anisotropic peak in wide-angle X-ray scattering (WAXS).[13] This peak indicates modulation in the electron density normal to the film surface. While this peak would be consistent with some tendency toward molecular layering, it does not allow a direct interpretation in terms of molecular orientation.

Here, we utilize spectroscopic ellipsometry to measure a number of important properties of IMC glasses vapor-deposited at $T_{\mathrm{substrate}}/T_g$ = 0.78, 0.84, and 0.90. The as-deposited glasses exhibited high kinetic stability and had densities 0.8−1.2% higher than the ordinary glass (OG) prepared by cooling the liquid at 1 K/min. Deposition at the

Received: March 16, 2012
Accepted: April 18, 2012
Published: April 18, 2012

higher temperatures yielded glasses with positive birefringence, while the lowest-temperature samples were negatively birefringent. These results establish, for the first time, that molecular orientation can be controlled while maintaining high density and high kinetic stability. The ability of the Lorentz–Lorenz equation to describe the relationship between the refractive index and the density is investigated here for high-density glasses. While the Lorentz–Lorenz equation is reasonably accurate for the SCL and OG of IMC, significant deviations can occur for the as-deposited glass.

Figure 1 shows the thickness changes that occur during temperature ramping at 1 K/min for IMC glasses prepared by vapor deposition onto substrates with three different temperatures. The initial heating provides the thermal expansion coefficient of the as-deposited materials (α_{AD}). Starting at T_{onset}, the materials undergo significant expansion (~ 2%) as they transform into the SCL. The samples were then cooled from 335 K, and the change in thickness with temperature characterizes the thermal expansion coefficient of the SCL, α_{SCL}. Near 310 K, the liquid is no longer able to structurally relax on the time scale of cooling, and a change in the thermal expansion coefficient is observed due to the glass transition; we refer to the glass prepared in this manner as the OG. A second heating and cooling was performed on each of the three samples, and these data are also shown in Figure 1. The initial stage of the second heating allows measurements of the thermal expansion coefficient for the OG (α_{OG}). The second heating and cooling curves show the expected hysteresis at T_g. The samples for which T_{sub} = 245 K were reheated to 325 K and recooled an additional five times (data not shown). These additional curves are indistinguishable for the data shown in Figure 1 and ensure that the as-deposited material fully transformed into the SCL. Values of T_{onset}, T_g, and the thermal expansion coefficients for the data sets shown in Figure 1 (and other experiments using the same deposition temperatures) are given in Table 1.

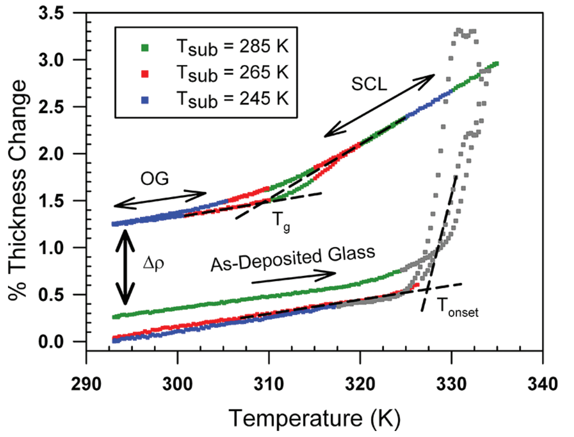


Figure 1. Thickness changes during temperature ramping for IMC glasses vapor-deposited at 285, 265, and 245 K. The as-deposited glasses are 0.8–1.2% more dense than the OG and are stable well above T_g for the ordinary glass. All three samples yield the same SCL upon transformation, as indicated by the excellent superposition of the blue, red, and green data sets; some segments of data have been removed to show this. Gray points indicate that the single-layer Cauchy model cannot adequately describe the ellipsometry data during the transformation into the SCL (see text). Data density has been reduced to 1/3 for clarity.

Table 1. Properties Obtained by Temperature Ramping Vapor-Deposited IMC

property	T_{sub} = 245 K	T_{sub} = 265 K	T_{sub} = 285 K	standard deviation[a]
α_{AD} (10^{-4} K^{-1})	1.32	1.39	1.27	0.08
α_{OG} (10^{-4} K^{-1})	1.28	1.33	1.33	0.06
α_{SCL} (10^{-4} K^{-1})	5.81	5.69	5.75	0.17
$T_{fictive}$ (K)	282	279	287	2
T_{onset} (K)	327	327	330	1
T_g (K)	309	309	309	1
$\Delta\rho/\rho_{OG}$ (%)[b]	1.24[c]	1.19	0.85[c]	0.02

[a] Standard deviations are computed for T_{sub} = 265 K and are assumed to apply at all substrate temperatures except where noted. [b] Determined at three incident angles. All other values are from single-angle measurements. [c] On the basis of a small sample set, we estimate the error to be ±0.05.

Figure 1 shows that vapor-deposited glasses of IMC have significantly higher densities than the OG. The glass deposited at 285 K has a density that is about 0.9% greater than the glass prepared by cooling the liquid at 1 K/min. It is insightful to describe the as-deposited glass in terms of a fictive temperature, $T_{fictive}$, that characterizes the density in comparison to the density expected for the SCL at temperatures below the ordinary T_g. This value can be obtained graphically from the (extrapolated) intersection of the thicknesses for the SCL and as-deposited glass in Figure 1. For samples deposited onto substrates at 285 K, $T_{fictive}$ is 287 ± 2 K, indicating that the as-deposited glass has nearly the density expected for the equilibrium SCL at the deposition temperature. During vapor deposition, molecules are able to efficiently search for low-energy packing configurations due to high mobility near the surface, if the substrate temperature is not too low.[14] It has recently been shown that surface diffusion on IMC is 10^7 times faster than bulk diffusion at 310 K, and a much larger ratio is expected at 285 K.[15] Continuous deposition traps these low-energy packing arrangements into the bulk glass.[16,17]

IMC glasses vapor-deposited at 265 and 245 K have even greater densities (~1.2%) relative to the OG prepared by cooling at 1 K/min. For the samples deposited at 265 K, $T_{fictive}$ determined by the density is 279 ± 2 K; a slightly higher value (286 ± 3 K) was measured previously by calorimetry on much thicker samples.[16] For an OG of IMC, we estimate that it would require at least 10^4 years of annealing or slow cooling in order to attain the same density as the sample vapor-deposited at 245 K.

We isothermally transformed samples deposited at 265 K to verify that the transformation path does not influence the density difference between as-deposited glass and OG. Representative data for transformations at 325 K are shown in the Supporting Information. The isothermal transformations yielded density differences consistent with the values obtained from temperature ramping experiments within 0.05%. The $\Delta\rho$ and $T_{fictive}$ values in Table 1 are from isothermal measurements for T_{sub} = 265 K and from temperature ramping experiments for T_{sub} = 245 and 285 K.

All of the vapor-deposited glasses shown in Figure 1 exhibit much higher kinetic stability than the OG, with T_{onset} exceeding T_g by about 20 K. For samples deposited at 265 K, isothermal transformation at 325 K required a total of 2700 ± 300 s, in good agreement with previous measurements by nanocalorimetry.[18] This transformation time is about 10^4 times larger than the α relaxation time for the SCL at this temperature.[19]

There have been reports that vapor-deposited organic glasses can transform into liquids with properties different than those expected for the equilibrium SCL.[9,20] The data in Figure 1 establish that the glasses formed at the three different deposition temperatures all transform into the same SCL, as seen by the excellent superposition of the OG/SCL curves. Table 1 shows that the SCLs formed from the three different vapor-deposited glasses have the same values of α_{SCL}, α_{OG}, and T_g. (See the Supporting Information for further discussion.)

The gray points in Figure 1 represent data for which the anisotropic Cauchy model is unable to accurately fit the ellipsometry data. It has been previously established that the transformation of a stable glass into a SCL occurs via a surface-initiated growth front mechanism.[21−23] For thin films, layers of SCL and stable glass coexist during the transformation. Because the SCL has a different index of refraction than the as-deposited glass, IMC cannot be modeled as a single optical layer in this regime. The fits to the ellipsometry data return to high quality when the transformation to the SCL is complete. Similar behavior has been observed in an elliposometric study of high-density glasses of *α,α,β*-trisnaphthylbenzene prepared by vapor deposition (unpublished data).

Both positive and negative birefringence values are obtained for IMC glasses vapor-deposited in the range of 245−285 K. Figure 2 shows the birefringence during temperature cycling, with the birefringence calculated as the difference between the out-of-plane and the in-plane indices of refraction ($\Delta n = n_z - n_{xy}$). Two samples for each substrate temperature are shown, demonstrating that independent depositions yield highly reproducible results. As each sample is heated, its birefringence is initially temperature-independent. As each sample reaches the onset temperature, the birefringence tends toward zero. As expected, the SCL is optically isotropic, and upon cooling, the OG is as well.

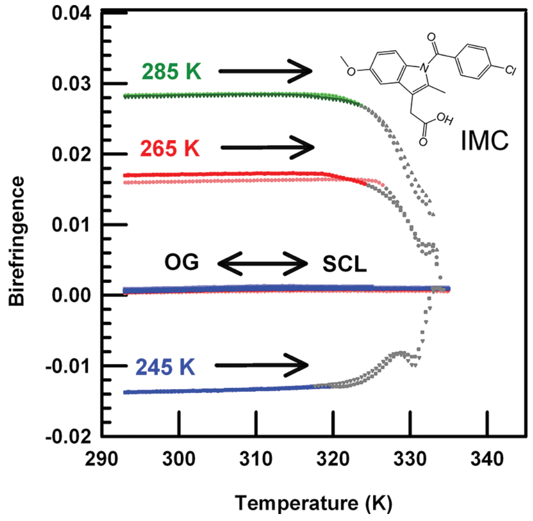


Figure 2. Optical birefringence during temperature ramping for IMC glasses vapor-deposited at 285, 265, and 245 K. The as-deposited glasses show both positive and negative birefringence. Sample to sample agreement is demonstrated by plotting two samples for each deposition temperature. As the as-deposited glass transforms into the SCL, the birefringence becomes zero within experimental error. Data density has been reduced to 1/5 for clarity.

These birefringence measurements, in combination with recent WAXS results,[13] indicate that an interesting range of local packing environments can be prepared by physical vapor deposition while maintaining high density and high kinetic stability. Birefringence in organic materials is typically interpreted in terms of molecular orientation.[2,24,25] For IMC samples deposited at 285 K, our results are consistent with a scenario in which the molecular axis with the maximum polarizability is more likely to be oriented along the surface normal. In contrast, deposition at 245 K predominantly places this axis in the plane. Dawson et al. reported that deposition of IMC at these two temperatures yields essentially identical (and substantial) anisotropic scattering peaks in WAXS experiments.[26] The lack of correlation between the birefringence and the anisotropy measured by WAXS indicates that many types of anisotropic order are consistent with high density and high stability.

There is a qualitative similarity between the birefringent glasses described here and those previously prepared from molecules used in OLED devices. Yokoyama and co-workers have vapor-deposited about a dozen OLED molecules and used ellipsometry to characterize the birefringence and dichroism of the resulting glasses.[12] For a few molecules, three different substrate temperatures were utilized, and for BSB-Cz (4,4′-bis[(*N*-carbazole)styryl]biphenyl), a birefringence trend similar to that observed for IMC was reported; the highest-temperature deposition produced positive birefringence, while lower-temperature deposition produced negative birefringence.[12] We note that BSB-Cz is a much more extended molecule than IMC and also that the absolute value of Δn was much larger for BSB-Cz (roughly +0.15 at the highest deposition temperature). Nevertheless, the qualitatively similar trends observed here and in ref 12 raise the prospect of preparing high-density, high-stability glasses for use in OLEDs if the correct substrate temperature is utilized.

Because ellipsometry provides access to the refractive indices and the densities of these vapor-deposited IMC glasses, we can establish the extent to which the Lorentz−Lorenz equation is consistent with our data. For isotropic materials, the Lorentz−Lorenz equation connects these quantities to the specific refractivity R

$$R = \frac{1}{\rho}\frac{n^2 - 1}{n^2 + 2} \tag{1}$$

In the Lorentz−Lorenz model, R is a material constant that is independent of temperature and the state of the system (gas, liquid, crystal, or glass). For anisotropic materials, this equation can be generalized[27] for uniaxial anisotropy to read

$$R_i = \frac{1}{\rho}\frac{n_i^2 - 1}{\langle n^2 \rangle + 2} \qquad i = xy,\, z \tag{2a}$$

$$\langle n^2 \rangle = \frac{n_z^2 + 2n_{xy}^2}{3} \tag{2b}$$

For crystals, the anisotropic specific refractivities provide access to the principal values of the polarizability tensor of the molecules.[24] The quantities R_z and R_{xy} are plotted in Figure 3 for an IMC glass deposited at 285 K that has been temperature-ramped in the manner described for Figures 1 and 2. The indices of refraction used in this calculation are available in the Supporting Information, as are R_z and R_{xy} for the other two deposition temperatures. Changes in thickness were converted to density by fixing the density of the OG at 293 K to its known value.[28]

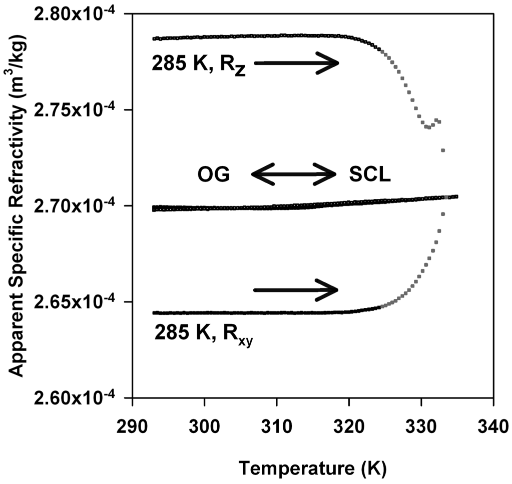


Figure 3. Anisotropic specific refractivities for a vapor-deposited IMC glass (285 K substrate temperature, $\lambda = 632.8$ nm) during temperature cycling. The near constancy of R_z and R_{xy} for the SCL and OG indicates that the isotropic Lorentz−Lorenz equation is valid to within about 0.3% for these isotropic states.

Figure 3 allows us to make several interesting observations regarding the utility of the Lorentz−Lorenz equation and its anisotropic extensions for IMC glasses and liquids. (1) For the SCL and OG, $R_z = R_{xy} = R$. Under this condition, eq 1 predicts that R is a constant. In our experiments, R varies by 0.3%, which is larger than the error in the data. To our knowledge, this is the first check on the validity of the Lorentz−Lorenz equation for a molecular glass-former traversing the glass transition. Above T_g, the Lorentz−Lorenz equation fails more significantly for some organic liquids.[29−31] (2) For the as-deposited glass, R_{xy} and R_z differ by 5%. This difference is expected given that the sample is birefringent. (3) If we form the isotropic average refractivity for the as-deposited glass, $\langle R \rangle = (2/3)R_{xy} + (1/3)R_z$, this quantity is about 0.3% lower than R for the OG. In this limited sense, the isotropic Lorentz−Lorenz equation retains some validity for the as-deposited glass. (4) If an experiment were to measure R_z during the temperature cycling of the as-deposited glass and use the isotropic Lorentz−Lorenz equation to predict the density change, one would interpret the data to indicate a 3% change in density, whereas the actual density change is about 1% (see Figure 1).

In summary, we have used spectroscopic ellipsometry to study the properties of three IMC glasses vapor-deposited between 0.78 and 0.90T_g. The as-deposited glasses exhibited high kinetic stability and density. Both positive and negative birefringence values were observed, indicating that high density and high kinetic stability are compatible with qualitatively different anisotropic distributions of molecular orientation. We observe qualitative similarity between the birefringence of these IMC glasses and previously reported results for a more extended molecule used in OLEDs. Understanding the local structures present in these glasses is a major challenge, and we anticipate that molecular simulations[32] will be useful in this regard.

■ EXPERIMENTAL METHODS

Amorphous films of IMC (550 nm; Sigma Aldrich, used as received) were prepared by physical vapor deposition in a vacuum chamber with a base pressure of $(3-5) \times 10^{-8}$ Torr. The substrates were silicon wafers in the ⟨100⟩ orientation with a native oxide coating and were attached to temperature-controlled copper fingers. The deposition rate for all samples was 0.18 ± 0.02 nm/s. Previous work has established that IMC films thicker than 300 nm exhibit bulk T_g values when cooled from the SCL.[33] The T_g for IMC measured by differential scanning calorimetry (10 K/min) is 315 K,[16] and this value has been used to calculate T_{sub}/T_g.

IMC samples were temperature-ramped at a rate of 1 K/min, and flowing nitrogen was used to minimize the water content of the sample. Measurements of the film thickness and the index of refraction were done with a spectroscopic ellipsometer (M-2000 V, J.A. Woollam Co., Inc.). The ellipsometric data for the IMC films were fit using an anisotropic Cauchy model in which the birefringence is wavelength-independent (see Supporting Information). The absorptivity in the Cauchy model was fixed to zero, and to meet this condition, we only fit data acquired at wavelengths between 500 and 1000 nm. Before and after transformation, ellipsometric data were taken at three incident angles (50, 60, and 70° from the normal). Data was acquired only at 70° during transformation. Measurements taken at three angles agreed with single-angle measurements within one standard deviation of the mean for T_{sub} = 265 and 245 K and agreed reasonably at T_{sub} = 285 K.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional figures and tables comparing temperature ramping and isothermal transformations along with the wavelength dependence of optical properties. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ediger@chem.wisc.edu. Phone: 608-262-7273.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under Award DE-SC0002161.

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