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Polymer processing techniques involving solvent vapor swelling are typically challenging to control and thus reproduce. Moreover, traditional descriptions of solvent swollen films lack microscopic detail. We describe the design and use of an apparatus that facilitates macroscopic and microscopic characterization of samples undergoing solvent vapor swelling in a controlled environment. The experimental design incorporates three critical characteristics: (1) a mass-flow controlled solvent vapor delivery system allows for precise control of the amount of solvent vapor delivered to the sample, (2) a sample prepared on a quartz crystal microbalance allows for real-time assessment of the extent of sample swelling, (3) a second sample prepared and assessed in parallel on a coverslip allows real-time fluorescence microscopy during swelling. We demonstrate that this apparatus allows for single-particle tracking, which in turn facilitates in situ monitoring of local environments within the solvent-swollen film. © 2016 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4939669]

I. INTRODUCTION

Polymers in contact with a compatible liquid- or vapor-phase solvent undergo swelling. Homopolymer swelling has been extensively studied theoretically and experimentally, and polymer swelling behavior has been exploited for applications including photolithography and ion exchange.1-5 In 1995, polymer swelling through exposure to solvent vapor was used as a tool for attaining long-range nanoscale ordering in diblock copolymer thin films in a process that became known as solvent vapor annealing (SVA).6 This approach has become a widely used alternative to thermal annealing for attaining order in such materials, as it is typically both milder and more efficient than thermal annealing.7,8 In recent years, there has been significant effort directed towards understanding and controlling the SVA process to attain better ordering in thin films of diblock copolymers as well as for bottom-up assembly of organic materials.7,9 Despite this, SVA remains poorly understood and of limited reproducibility, with conditions set empirically for individual applications by individual laboratories.7

Polymer swelling is a complex phenomenon. In the homopolymer case, swelling comprises two competing phenomena, solvent diffusion through the polymer and relaxation of the polymer.5 The relative rates of solvent diffusion and host relaxation determine the details of the solvent swelling process as well as the molecular rearrangements that occur upon swelling. For example, polymers in a thin film prepared by spin-coating have been shown to reptate following swelling with a good solvent.10,11 When applied to diblock copolymers, the aforementioned complexities are exacerbated by phase segregation of the individual blocks into nanostructures.7,12,13 While SVA clearly enhances the microphase segregation in these systems, allowing for long range order to be achieved, the ways in which solvent choice, vapor pressure, and degree and time course of swelling can be used to enhance and control this ordering remain unclear.

A key limitation to developing a fuller understanding of the SVA process is the limited capacity to monitor the process in situ. It is relatively straightforward to monitor degree of solvent uptake in a polymeric thin film via quartz crystal microbalances (QCMs) or optical metrology techniques.4,5,14-18 QCMs operating in dissipation mode could additionally report bulk viscoelastic properties of a film during the process.15 Evolving structural changes and potential inhomogeneity of structure and mechanical properties across the films over time are more challenging to assess during SVA. For diblock copolymers, grazing incidence small-angle x-ray scattering (GISAXS) has been used to assess transient nanostructures that arise during swelling.12,13,19-22 While GISAXS can reveal nanostructural motifs present in a swollen film, it cannot describe molecular motions in a spatially resolved manner. Indeed, no study to date has simultaneously assessed film thickness and local structure or dynamics in real time. Moreover, most of the aforementioned studies did not quantitatively control solvent vapor pressure, limiting ability to reproduce findings and generalize results.

Here, we describe an apparatus for controlled delivery of solvent vapor to polymer thin film samples and simultaneous monitoring of multiple properties of those samples throughout the process of solvent vapor annealing. To achieve this multi-modal monitoring, two polymer thin films are prepared in an identical fashion and assessed in parallel adjacent to each other within a single sample chamber. One sample, prepared...
on a QCM, is used to characterize the extent of swelling while another, prepared on a coverslip, is used for epi-fluorescence imaging. Swelling is performed in a controlled fashion using a series of mass-flow controllers (MFCs) to generate and control solvent vapor pressures. This approach to studying polymer films in their vapor swollen state allows simultaneous characterization of film swelling, viscoelasticity, structure, and/or dynamics under well-controlled conditions.

We demonstrate the broad utility of information that can be accessed using this apparatus via two proof-of-principle experiments. In one case, the dynamics within a polymer thin film are characterized by particle-tracking quantum dot (QD) dopants, data that illuminate both bulk enhancement of diffusion that occurs upon swelling as well as heterogeneity in dynamics across the swollen film. In a second example, a mixture of solvents is used to monitor the aggregation of conjugated polymer guests, demonstrating that the control of the conditions in the sample chamber is sufficient to direct bottom-up assembly of mesoscopic structures.

II. APPARATUS

A. Solvent vapor annealing chamber

The sample chamber is composed of three parts—the base, the body, and the lid—machined from aluminum. Within the sample chamber, two polymer thin films were prepared and assessed in parallel, with a coverslip-mounted sample at the chamber base and a QCM-mounted sample at the chamber lid (Fig. 1). The base has an opening to hold a 25 mm diameter coverslip, sealed with Kalrez O-rings. The sample chamber lid is designed such that it can be fastened between the QCM crystal holder head and the retainer cover that holds the QCM in place (Fig. 1(c)). The QCM sensor lies above and concentric to the imaged sample. An inlet and outlet for vapor flow were bored through the sides of the cylinder body to allow connection to a MFC-regulated vapor flow system. The inlet and outlet to the sample chamber are controlled by two pin valves. The three components of the sample chamber are held together with bored-through screws with intercalating Kalrez O-rings to assure a good seal. In the experiments performed here, Teflon tape was applied around all junctures to further protect against possible leaks.

B. Solvent vapor production

Solvent vapor was generated using a series of mass-flow controllers (Alicat Scientific MCS-100) to bubble dry nitrogen carrier gas through solvent reservoirs. In the configuration shown in Fig. 2, two MFCs (MFC-A and MFC-B) control flow in two channels, though this system can be extended to more channels to support delivery of complex mixtures of solvents. A switch is present in each channel (S-A and S-B in Fig. 2) to allow bypassing of the solvent reservoir connected to that channel. The flow of each channel is combined in a mixing bottle to assure a reservoir of equilibrated vapor mixtures. Downstream from the mixing bottle, another switch (S-C) allows flow to or bypass of the sample chamber. Perfluoroalkoxy tubing (McMaster Carr; Ultraclear PFA Tubing, 1/8 in. inner diameter) was used to connect all the components involved with solvent vapor production and delivery since it is extremely resistant to a wide range of organic solvents.

C. Sample characterization

The sample at the bottom of the chamber was prepared on a coverslip and was interrogated via wide-field epi-fluorescence microscopy. The exemplary experiments described here employed continuous wave 488 nm excitation,
an oil-immersion objective lens (Olympus PlanApo N 60×, NA = 1.4), and appropriate dichroic (488 nm), longpass (520 nm), and bandpass (525-675 nm) filters. Images were collected using an EMCCD camera (Andor iXon DV-855).

In theory, the film employed for imaging could also be used to monitor film swelling through an optically based technique such as ellipsometry or interferometry. However, doing so could complicate fluorescence imaging; moreover, the film to be imaged must be prepared on a coverslip, which is not ideal for these approaches. Instead, film thickness and swelling were assessed via parallel measurements on a film prepared on the QCM (Stanford Research Systems QCM-200) at the sample chamber’s top. This measurement does not interfere with imaging, and the QCM is compact and simple to operate. Moreover, the QCM can return information on film viscoelasticity that can be used to validate storage and loss moduli obtained, for example, via particle tracking microrheology on the coverslip-mounted film. The QCM should be operated in a mode that corrects for resonance frequency changes due to viscoelastic losses.

III. CONTROL OF VAPOR PRESSURE

A. Single solvent delivery

As depicted in Fig. 2, solvent vapor was generated using MFCs to bubble dry nitrogen gas through solvent reservoirs. To assess the system’s performance, expected and actual amounts of generated acetone vapor were compared. The flow controllers allow direct control of Q, the volumetric flow rate. The following equation describes the relationship between volumetric and molar flow rate:

$$M = \frac{Q \rho}{MW},$$

where $M$ is the molar flow rate, $Q$ is the volumetric flow rate, $\rho$ is the gas density, and $MW$ is the molecular weight of the gas. For nitrogen gas, employing $Q_{\text{nit}} = 100$ standard cm$^3$/min (sccm) yields $M_{\text{nit}} = 4.147 \times 10^{-3}$ mol/min. At this flow condition, the Reynolds number in the tubing used is 177, indicating laminar flow.

To calculate the molar flow rate for the solvent vapor, several assumptions were made. First, it was assumed that bubbling nitrogen gas through a solvent promotes solvent evaporation, ensuring that solvent vapor pressure remains at saturation ($p_{\text{sol}}$) for a given temperature. Because the solubility of nitrogen in common solvents is negligible, it was also assumed that $M_{\text{nit}}$ remains constant after bubbling. Finally, the total pressure in the system was assumed to be 760 Torr because the SVA is an open system with low flow rates. Given these assumptions, the molar flow rate for solvent vapor ($M_{\text{mol}}$) for a MFC-controlled channel is given by

$$M_{\text{mol}} = M_{\text{nit}} \left[ \frac{p_{\text{sol}}}{760 - p_{\text{sol}}} \right].$$

![Schematic diagram of the solvent vapor delivery system. MFCs control the flow of carrier gas through the appropriate solvent reservoirs and the sample chamber. Switches and valves are present throughout (indicated by S- and V-, respectively) to direct and control flow. The vent at right is left open except in cases where the solvent trap is used to condense solvent vapors to assess quantity of solvent that was delivered to the sample.](image-url)
Since \( p_{\text{acet}} = 193.19 \text{ Torr at } 21^\circ \text{C}, \) for \( Q_{\text{acet}} = 100 \text{ sccm}, \) a volumetric flow rate of \( Q_{\text{acet}} = 93.51 \mu \text{L/min} \) was expected. Experimentally, over two trials, \( 1760 \pm 110 \mu \text{L acetone was recovered at the solvent trap when nitrogen gas flowed at } Q_{\text{acet}} = 100 \text{ sccm for 20 min and bubbled through acetone. This volume corresponds to } Q_{\text{acet}} = 88 \pm 5 \mu \text{L/min.} \) With a deviation of less than 10% between predicted and measured recovered solvent, it was assumed there were no significant leaks present in the system.

In a single channel configuration such as that described above, altering \( M_{\text{acet}} \) will alter the rate of swelling, but the equilibrium vapor pressure in the chamber will be the saturated vapor pressure of the solvent regardless of \( M_{\text{acet}}. \) The film is thus expected to swell to the same degree over a range of nitrogen mass flow rates. To lower the vapor pressure of the delivered solvent relative to the saturated vapor pressure and decrease degree of film swelling, mass flow of nitrogen through the solvent can be lowered while keeping the total nitrogen mass flow rate identical by using the second MFC to deliver additional nitrogen gas to the chamber (bypassing the second solvent container). The vapor pressure at the sample is then given by

\[
p = p_{\text{sol}} * M_{\text{sol}} / M_{\text{tot}}.
\]

where \( M_{\text{tot}} \) includes that delivered through the solvent as well as that delivered directly to the chamber.

We demonstrate these two methods of controlling flow rate and vapor pressure using poly(methyl methacrylate) (PMMA) films swollen with toluene vapor. The films were prepared by spin-coating 3.4 wt. % solutions of PMMA (Sigma Aldrich, \( M_{\text{w}} = 350,000 \text{ g/mol} \)) in toluene onto sample substrates (coverslip and QCM) at 2000 rpm. Prior to the swelling experiments, solvent vapors were equilibrated by bubbling carrier gas through the appropriate solvent reservoirs and bypassing the sample chamber for 30 min. In addition, the arm of the QCM was allowed to mechanically equilibrate for at least 2 h and parasitic capacitance was cancelled.

Initial film thickness was assessed via change of QCM frequency as described by Eqs. (1) and (2). Over nine samples, the change in resonance frequency of the QCM after spin-coating was \( 1427 \pm 65 \text{ Hz}, \) corresponding to film thickness of \( 213 \pm 10 \text{ nm}. \) This value was corroborated by subjecting a sample prepared in the same way to scratch analysis on an atomic force microscope (AFM), which yielded a thickness of \( 215 \text{ nm}. \)

Swelling of the PMMA films with toluene vapor was then performed, varying either the toluene vapor pressure in the chamber or the mass flow rate of the toluene. First, nitrogen was bubbled through toluene in one channel, and a second channel was used to dilute the vapor with carrier gas. In these experiments, overall flow rate was kept constant at \( 100 \text{ sccm}. \) Ultimate degree of swelling was expected to differ as the solvent vapor pressure varied with the mass flow of nitrogen through the solvent as described by Eq. (5). The expected behavior was observed, as was the fact that extent of swelling did not change linearly with partial toluene vapor pressure (Fig. 3, solid lines). This is in accordance with the previous studies that showed a non-linear decrease in the glass transition temperature for polymers undergoing vapor swelling, with the effect more dramatic at higher solvent weight fractions.

Next, the rate of swelling was varied by controlling the solvent delivery rate. To accomplish this, a single channel was used to bubble nitrogen gas through toluene, and flow rate was varied. An example is shown in Fig. 3 for a scenario in which saturated toluene vapor was delivered at 50 sccm (red dotted line) compared to at 100 sccm (red solid line). This led to a slower rate of swelling, as expected.

In this set of experiments and similar experiments with different solvents that substantially swell the polymeric film, oscillations in apparent film thickness were sometimes evident. Visual observation of these samples after removal from the SVA chamber suggested that these oscillations were related to film de-wetting. Films studied here became susceptible to de-wetting under conditions in which the film swelled to greater than 1.5 times the initial film thickness, likely due to the solvent altering the surface-substrate interaction.

**B. Solvent mixtures**

Mixtures of solvents are appropriate for some experiments, including attaining order in diblock copolymer films and preparing aggregates of conjugated polymers. Such solvent mixtures can be delivered to a sample using either a solvent mixture in a single reservoir or pure solvents in separate reservoirs. We demonstrated ability to control and monitor vapor pressure in each scenario for a mixture of acetone and chloroform.

To demonstrate the expected dependence of vapor volume ratio on liquid volume ratio, mixtures of acetone and chloroform were prepared in a single solvent reservoir and flow rate was set at \( Q_{\text{acet}} = 100 \text{ sccm}. \) The generated vapors were condensed at the solvent trap and subsequently analyzed by gas chromatography. The resulting liquid–vapor equilibrium curve for acetone-chloroform liquid solvent mixtures is shown in Fig. 4(a). The vapor volume ratio differs from the liquid volume ratio in accordance with the boiling points of each
FIG. 4. (a) Liquid-vapor equilibrium curve for acetone-chloroform liquid solvent mixtures in a single reservoir. Error bars are standard deviations over 3 independent measurements, though most are smaller than the data points. (b) Experimental (blue) and calculated (red) chloroform vapor volume ratio as a function of \( Q_{\text{vit, tot}} \) at the chloroform channel for acetone-chloroform solvent vapor mixtures with the two solvents in separate solvent reservoirs and \( Q_{\text{vit, chl channel}} = 100 \text{ sccm} \).
The multi-modal aspect of the SVA system was exploited to explore aggregation of single polymer chains in swollen films in real time. Here, poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) synthesized as described previously\textsuperscript{16} ($M_m = 168\,000\,g/mol$, $PDI = 2.1$) was embedded in PMMA (Sigma-Aldrich, $M_m = 97\,000\,g/mol$). Sample films were prepared by spin-coating a toluene solution of MEH-PPV containing 6.0 wt. % PMMA on the QCM sensor and the coverslip at ~2800 rpm for 60 s. The dried films had MEH-PPV concentration of $\sim 5 \times 10^{-7}\,M$ and were determined to have a thickness of $\sim 270\,nm$ via Eqs. (1) and (2). Change in film thickness over the course of SVA was calculated from measured change of mass per unit area of the film combined with known vapor volume ratio and independent measurements of film swelling with each of the two solvents to determine swelling capacity of the PMMA film with these solvents.

The sample films were then placed in the chamber and exposed to nitrogen gas flow at $Q_{\text{in}} = 400\,scm$ for 30 min to remove residual solvents. Following this, the films were swollen with solvent vapor using an acetone–chloroform solvent mixture in a single container. The liquid volume ratio was 50:50, resulting in a vapor volume ratio of 56.3%:43.7%, as shown in Fig. 4(a). Aggregates were prepared using two different solvent swelling conditions, one in which the acetone-chloroform mixture was delivered at saturated equilibrium vapor pressure and the one in which the vapor pressure was at 85% of the saturation level.

Polymer film swelling and aggregation of MEH-PPV molecules were monitored simultaneously. Figures 6(a) and 6(b) show degrees of film swelling as measured at the QCM together with wide-field fluorescence images taken of the sample during swelling. Since the fluorescence intensity of single chains is low compared to emission from aggregates, the illumination intensity ($0.7\,W/cm^2$ at the sample) was chosen to best show the progression of aggregate formation rather than to allow visualization of single molecules.

Before solvent vapor exposure, the film exhibited moderate, largely homogeneous fluorescence as a result of many individual MEH-PPV chains dispersed within the film. The film was then swollen using the acetone-chloroform mixture as described above. Acetone is a selective solvent for the host PMMA matrix (having a Flory–Huggins interaction parameter of $\chi_{55} > 0.5$ for the host and $\chi > 0.5$ for MEH-PPV), thus swelling the host matrix allowing for diffusion of MEH-PPV chains. Mixing this solvent with chloroform, a non-selective solvent for the host polymer film swelling $B$. Monitoring and controlling aggregation during polymer film swelling

in Fig. 5(a) (gray line), and it overlaps well with that obtained from the QDs in the dry film. This sets a lower bound on the diffusion constant that can be reliably obtained from this experiment at $\sim 10^{-5}\,\mu m^2/s$.

Upon swelling of the PMMA with 75% of saturated toluene vapor pressure at $21^\circ C$, the QD probes attained a degree of mobility due to rearrangement of the surrounding host polymer and/or QD diffusion in the free volume within the film. The motion of one such QD is shown in Fig. 5(b), along with a track depicting its motion over 8 s in the fully swollen film, as reported by the QCM trace. The MSD for this QD as well as several others (thin red lines) and the ensemble average of all QDs tracked (thick red line) are shown in Fig. 5(a). We note that some very fast QDs were not trackable due to the decrease in signal to background ratio that occurs when the photons emitted during the exposure time ($0.2\,s$) are spread over a large area. The ensemble MSD was fit to a line yielding an average diffusion constant of the QDs in the film, $D = 5.2 \times 10^{-3}\,\mu m^2/s$, consistent with expectation for a polystyrene film with $\sim 30\%$ mass solvent.\textsuperscript{17} Importantly, the variation among individual QD MSDs suggests that the film is inhomogeneously mobile and that local viscoelasticity varies on the micron length scale in these swollen films. Particle tracking microrheology could then be used to characterize the variation in viscoelasticity as a function of position within the swollen film.

B. Monitoring and controlling aggregation during polymer film swelling

The multi-modal aspect of the SVA system was exploited to explore aggregation of single polymer chains in swollen films in real time. Here, poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) synthesized as described previously\textsuperscript{16} ($M_m = 168\,000\,g/mol$, $PDI = 2.1$) was embedded in PMMA (Sigma-Aldrich, $M_m = 97\,000\,g/mol$). Sample films were prepared by spin-coating a toluene solution of MEH-PPV containing 6.0 wt. % PMMA on the QCM sensor and the coverslip at $21^\circ C$ yielding an average di

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consistent with Ostwald ripening,\textsuperscript{39–42} in which single polymer chains preferentially re-solvate from smaller aggregates and are incorporated into larger aggregates, as has been suggested previously.\textsuperscript{28} While the two films have approximately the same number of aggregates 10 min into swelling, when the films are equally swollen, by 20 min it is evident that the film that is more swollen has fewer aggregates, suggesting that the aggregation process is limited by diffusivity of the single molecules and/or small aggregate species. While the degree of film swelling saturated after \textasciitilde{}20 min of solvent vapor swelling, aggregate growth continued during the entire time the film was swollen, as judged by both the decreasing number of features and the increasing brightness of the imaged spots. Assuming the density of MEH-PPV chains is similar regardless of aggregate size, aggregate size will be correlated with fluorescence intensity.\textsuperscript{28} Figure 6(d) shows histograms for the fluorescence intensity of individual aggregates after 50 min of solvent swelling of the film, with intensity calculated by averaging intensities of the 5 brightest pixels in each feature. Aggregates generated under the higher partial vapor pressure exhibited higher fluorescence intensity, reflecting their larger size. Such aggregates could be further characterized over the course of the swelling and de-swelling process by quantifying fluorescence intensity, fluorescence anisotropy, and/or emission spectra. These results, in which aggregates formed in a given time differ in size as a function of saturated vapor pressure delivered, hint at the prospect of controlling not only aggregate size but also photophysical properties such as fluorescence anisotropy and spectra through precise control of the solvent swelling process.

V. CONCLUSION

Solvent vapor annealing studies to date have been limited in their ability to simultaneously control and monitor extent of swelling while characterizing film microscopic structure and dynamics. We accomplish such control and measurement here by using mass-flow controllers to set solvent vapor pressures, a quartz crystal microbalance to characterize film swelling, and an epi-fluorescence microscope to characterize structure and dynamics within the film. This approach enables both the study of solvent vapor annealing processes and controlling the processes mediated by the solvent-swollen phases of polymer films.

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