

Anomalous Temperature Dependence of Solvent-Enhanced Dye Diffusion In Polymer Films

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ABSTRACT

One promising method to pattern full color polymer Organic Light-Emitting Diode (OLED) displays is to print dye from a pre-patterned organic film onto a spin-cast polymer and then diffuse the dye into the film at room temperature in a solvent vapor environment. This method utilizes the well-known tendency for a polymer film to absorb solvent vapor, which depresses the glass transition temperature of the polymer and dramatically increases diffusion of the dye. In this work, we have studied the temperature dependence of this process. The dye coumarin 6 (C6) was transferred onto films consisting of 2-(4-biphenyl)-5-(4-tert-butyl-phenyl)-1,3,4-oxadiazole (PBD) mixed with the polymer poly(9-vinylcarbazole) (PVK). Samples were then placed on a heated stage in a chamber and exposed to acetone vapor to diffuse the C6 into the polymer film. The profile of the diffused dye was determined by depth-dependent photoluminescence measurements and Secondary Ion Mass Spectroscopy. We observed that the amount of diffused dye decreased at higher temperatures, in contrast to conventional thermally-driven diffusion. The results are understood by noting that the decrease in the polymer glass-transition temperature and the corresponding rapid increase in dye diffusivity depend on the quantity of solvent absorbed by the polymer, which decreases as the temperature of the polymer is raised.

INTRODUCTION

The desire to fabricate large-area Organic Light-Emitting Diode (OLED) displays has been a central research goal in recent years. One of the important challenges is the development of a suitable process to pattern individual OLED pixels to emit light at different wavelengths to achieve a full color display. The approach taken depends on whether the active material in the OLED is a small molecule (molecular weight several hundred grams/mole) or a polymer. Since small molecule OLEDs are typically fabricated by thermally evaporating the small molecule to form a film on the substrate, a shadow mask may be used to locally pattern these devices. However, polymer films are traditionally deposited by spin-casting because their high molecular weight inhibits thermal evaporation. This process leaves a homogenous film emitting at only one color.

One of the strategies to pattern polymer-based OLED displays is to deposit the polymer by other means. Examples of such efforts include inkjet printing [1] and screen printing [2]. An alternative strategy that retains the deposition of polymer films by spin-casting relies on dyes that, when added to the polymer matrix in very small concentrations (~1 wt %), change the emission spectrum of the film. One method employing this approach has been introduced in previous papers and is illustrated in Figure 1 [3]. In step 1 a pre-patterned dye source and target spin-cast polymer film are placed in intimate contact and heated to transfer the dye from the source to the target film. This printing step can be repeated with different dyes to pattern pixels

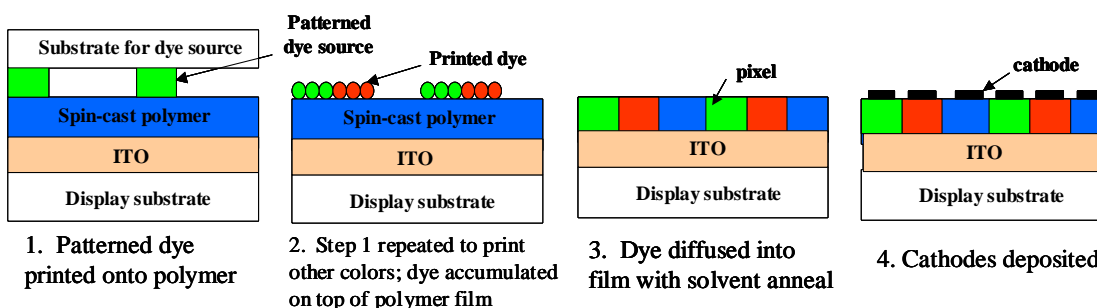


Figure 1. Schematic diagram of dye printing and solvent anneal process to fabricate full-color polymer OLED displays [3,4].

of different colors, and leaves the dye accumulated on the top of the polymer film (step 2). The dye must then be diffused into the polymer film in step 3 to affect the local emission color of the film. Finally, in step 4 cathodes are deposited to complete the fabrication of the display.

The dye diffusion in step 3 is crucial for efficient color emission. However, the dye diffusion coefficient in most polymer device layers is low because these polymers are chosen to have a high glass-transition temperature (T_g) for device stability. In order to completely diffuse the dye throughout the film with a conventional thermal anneal, high temperatures ($> 100^\circ\text{C}$) and long anneal times (several hours) can be required. The damage caused to the polymer film during such a process can lower device efficiency. Therefore, a solvent-enhanced diffusion process that provides uniform distribution of the printed dye throughout the polymer film at room temperature has been developed [4,5]. The process relies on the well-known tendency for polymer films to absorb certain solvent vapors, which causes a depression of T_g [6]. As T_g is lowered, the polymer softens and dye diffusion can take place rapidly, even at room temperature. Following diffusion, the solvent vapor is removed and the film re-acquires its original mechanical stability. Efficient three-color OLEDs integrated in this manner have been demonstrated [7].

EXPERIMENT

In this work, we have examined the temperature dependence of dye diffusion in a polymer that is exposed to solvent-vapor. A schematic of the experimental apparatus is detailed in Figure 2. Samples were mounted on a resistively-heated stage in a glass cylinder and exposed to constant flows of a mixture of nitrogen and a solvent vapor obtained by bubbling nitrogen through the

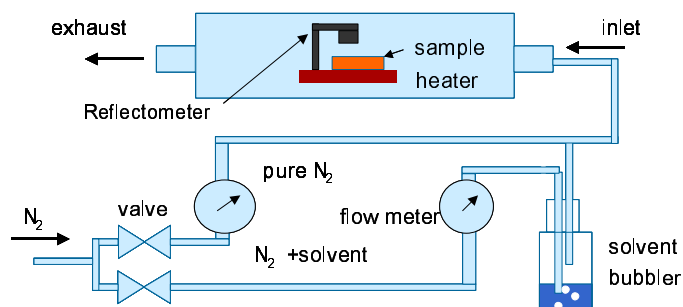


Figure 2. Diagram of experimental apparatus for solvent vapor anneals vs temperature [8].

solvent. A Filmetrics F20 Reflectometer mounted in the chamber was utilized to make *in situ* measurements of sample film thickness.

The polymer films consisted of the hole-transport polymer poly(9-vinylcarbazole) (PVK, M_w ca. 1,100,000 g/mol) blended with the small molecule electron-transport material 2-(4-biphenyl)-5-(4-tert-butyl-phenyl)-1,3,4-oxadiazole (PBD). 100 nm thick films were prepared by spin-coating solutions containing PVK (71 wt%), PBD (28.2 wt %), and the dye coumarin 47 (C47, emission peak at 440 nm, obtained from Lambda Physik) (0.8 wt %) onto sapphire substrates [9]. Source films of the polymer Vylon 103 (obtained from Toyoba) (98 wt%) containing the dye coumarin 6 (C6, emission peak at 580 nm, Aldrich) (2 wt%) were placed in contact with the PVK films in a vacuum oven and heated at 64° C for 20 minutes to transfer C6 onto the surface of the PVK films. Next, the PVK films were placed in the solvent vapor apparatus and exposed to a constant flow of 4.9 l/min nitrogen (partial pressure 640 torr) and acetone vapor (partial pressure 120 torr). The exposure lasted for 2 minutes, during which time the substrate was held at a constant temperature.

The effect of substrate temperature on the dye diffusion process was evaluated by depth-sensitive photoluminescence (PL) measurements. The absorption length of 254 nm UV radiation in PVK is only 50 nm, which allows selective probing of the bottom of the PVK/PBD film through the UV-transparent sapphire substrate [10]. The photoluminescent (PL) spectra of the bottom of films that were annealed at three different temperatures and an untreated film are shown in Figure 3. The C47 was dispersed uniformly throughout the film during the spin-casting process, so its peak is used to normalize each spectrum in order to correct for potential differences in substrate absorption. The size of each C6 peak indicates the relative amount of dye that has diffused from the top of the PVK/PBD film through to the lower 50 nm of the film. This peak is highest for the substrate held at 20° C, and lowest for the one held at 35° C during the vapor anneal.

Contrary to expectations based on conventional thermally-driven diffusion, this data indicates that the C6 dye has diffused less at higher temperatures. This trend was confirmed with Secondary Ion Mass Spectrometry (SIMS) analysis on a similarly treated set of samples. In this analysis, the sulfur atom located on the C6 molecule is used as a marker for the amount of C6 dye that is present at each depth in the PVK/PBD film. Figure 4 plots the sulfur signal obtained for samples following acetone anneals at 19° and 35° C, as well as the sulfur signal of a sample on which the C6 was printed but which received no further treatment. It is apparent that the 19° C anneal has caused the dye to diffuse nearly uniformly throughout the polymer film. In contrast, the dye in the sample annealed at 35° C is concentrated at the film surface and is only slightly more uniform than the as-printed profile.

Diffusion coefficients were extracted from the SIMS data by fitting Gaussian distributions to the sulfur profiles using the diffusion coefficients as an adjustable parameter. The “knock-on” effect, in which the Cs^+ probe beam displaces sulfur atoms towards deeper depths during measurement creating a broadening of the actual sulfur concentration, was ignored for simplicity. The calculated solvent-enhanced diffusion coefficients are plotted vs $1000/T$ in Figure 5. For comparison, diffusion coefficients obtained from thermally-annealed samples are included [4]. Two features of the plot are noted. The first is the enormous increase in diffusion enabled by the solvent vapor. Extrapolating the thermal diffusion data to room temperature we obtain a diffusion coefficient of $\sim 10^{-30}$ cm²/s, which is almost twenty orders of magnitude less than the room temperature diffusion coefficient in acetone vapor. The second feature is that the temperature dependence of the solvent-enhanced diffusion is opposite that of normal diffusion,

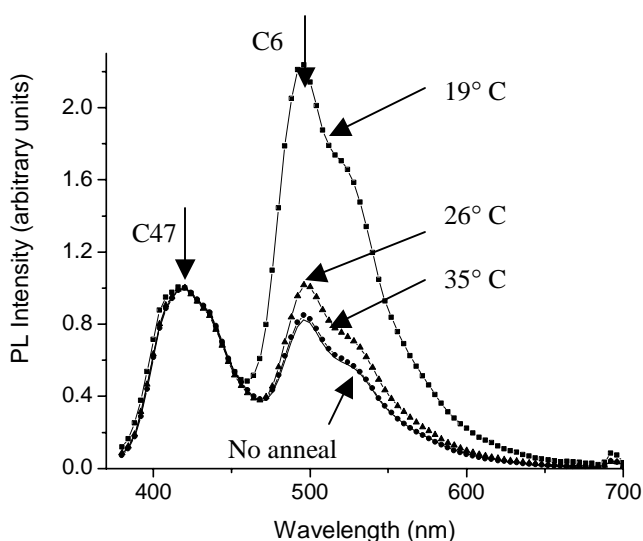


Figure 3. PL spectra of PVK/PBD films (measured through the sapphire substrate) that have been annealed in acetone vapor at different temperatures after dye printing. The spectrum of a device that has not been annealed is included and lies almost directly below the spectrum of the 35° C sample. All spectra have been normalized to the C47 emission peak.

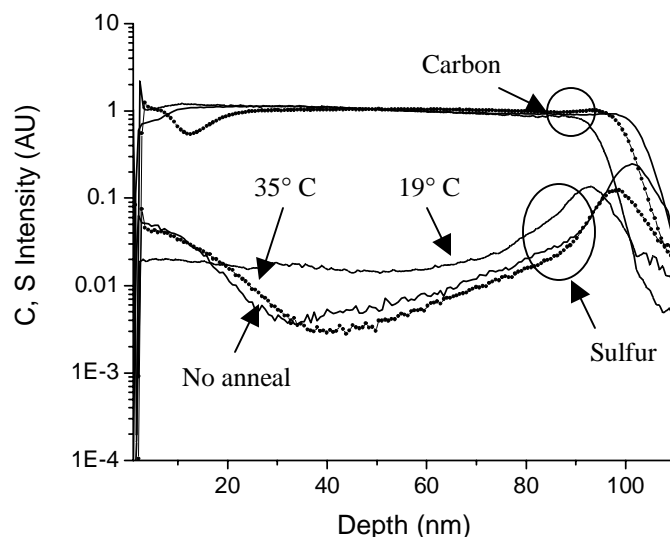


Figure 4. SIMS analysis of PVK/PBD films following printing of C6 dye and acetone anneals at 19°C and 35°C. The sulfur traces indicate the amount of C6 dye in each sample. The width of the carbon signal (from the host matrix) confirms the film depth of 100 nm. The dye is distributed uniformly at 19°C; very little diffusion takes place at 35°C. The sulfur-signal rise starting at a depth of 50 nm is thought to be O₂ from the substrate.

i.e. the diffusion of the dye is much greater at 19°C than at 35°C when the solvent vapor is present. Although only two points were evaluated by SIMS for quantitative extraction of diffusion coefficients, the qualitative luminescence data of Figure 3 clearly show an intermediate point at 26° C that confirms the unusual temperature trend.

DISCUSSION AND ANALYSIS

This striking behavior illuminates the importance of the solvent vapor in solvent-enhanced diffusion. At its most basic level, diffusion of a small molecule in a polymer film is dependent on the existence of free spaces in the film that are comparable in size to the molecule. Hence, diffusion rapidly increases as the temperature climbs above T_g and the polymer enters a rubbery phase characterized by a significant increase in free volume. Above the glass transition temperature, the dye diffusion coefficient D can be described by a modified form of the equation developed by William, Landel and Ferry (WLF-equation):

$$\log D = \frac{c_1(T - T_g)}{c_2 + (T - T_g)} + \log D_g, \quad (1)$$

where c_1 is a constant, c_2 a constant generally set equal to 51.6 K, and D_g the diffusion coefficient at T_g [11]. From equation (1), it is clear that diffusion can be raised by either increasing T or decreasing T_g . T_g for a polymer blend having components with volume fractions w_i and glass transition temperatures T_{gi} has been shown empirically to be given by [12]

$$\frac{1}{T_g} = \sum_i \frac{w_i}{T_{gi}} \quad (2)$$

Therefore, T_g can be decreased by the absorption of solvent vapor (having a low T_g) to the polymer blend. For example, the PVK (72 wt %) / PBD (28 wt%) blend has been measured to have a T_g of 125°C (as compared to 219°C for pure PVK) [4]. We estimate T_g for acetone by using the common approximation that T_g of a solvent is two-thirds its melting temperature (178 K for acetone) to obtain a $T_{g,acetone} = 119$ K [6,13]. Film thickness measurements of PVK/PBD films at room temperature in acetone vapor (partial pressure = 120 torr) indicate an increase in volume of the PVK/PBD film of 25%. Estimating that the increase in volume is equal to the volume of acetone absorbed, we calculate that T_g of the blend has been lowered to -5°C, a reduction of 130°C. A similar calculation using the observed volume increase of ~5% at 35°C yields a far smaller reduction in T_g of 45°C. Further work is underway to quantitatively match this reduction in T_g with the measured change in the dye diffusion coefficient.

The amount of acetone absorbed by a polymer leading to the swelling will depend on the kinetic balance between adsorption of the vapor by the polymer and the competing tendency for the solvent molecules to desorb and re-enter the vapor phase. Because the desorption process is expected to increase strongly at higher temperatures, the equilibrium at higher temperatures is expected to shift to less solvent contained within the polymer, leading to less swelling and less of a reduction of T_g . This rapid decrease of the polymer swelling was confirmed by *in situ* optical reflectometry measurements of the PVK/PBD film thickness in acetone vapor as a function of substrate temperature. Figure 6 plots these results. Since the swelling of the PVK film is dependent on the amount of acetone it absorbs, the decrease in PVK film thickness with temperature provides strong evidence of a decrease of acetone volume fraction.

The effect of increased temperature on the diffusion coefficient is therefore dependent on

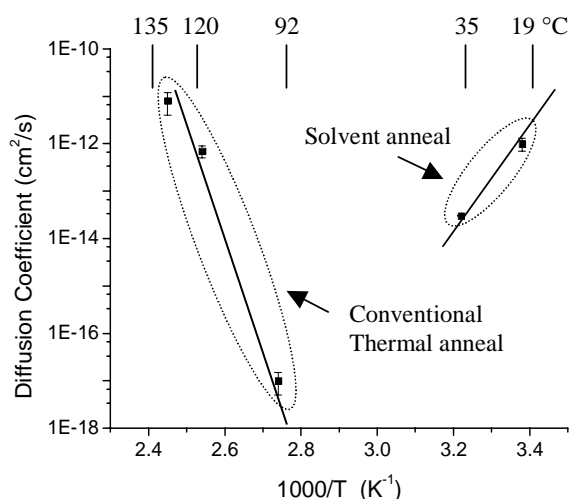


Figure 5. Acetone-enhanced diffusion coefficients for C6 in PVK/PBD films (extracted from SIMS data of Figure 4) and thermal diffusion coefficients in a vacuum environment ([4]) plotted vs. $1000/T$. The different diffusion conditions result in opposite dependences on temperature. Lines through the data points are intended to guide the eye.

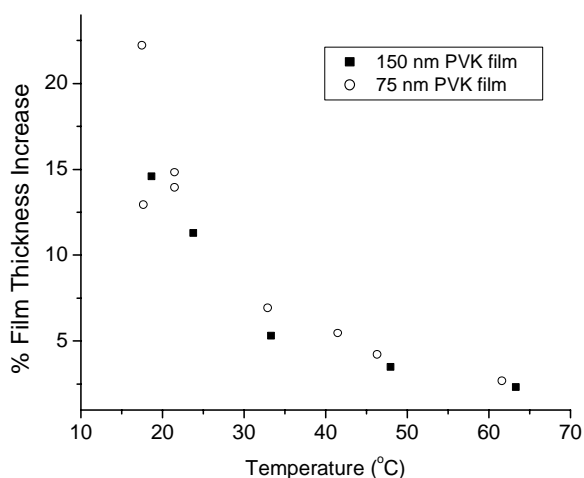


Figure 6. *In situ* measurements of the PVK/PBD film thickness increase in acetone vapor (120 torr) as a function of PVK/PBD temperature for as-deposited film thicknesses of 75 nm and 150 nm. The polymer film thickness decreases roughly exponentially with temperature.

two competing trends. The first is the increased thermal motion of the polymer and dye molecules, resulting in an increase in free volume available for diffusion and increased movement of dye molecules into available free space. The second is an exponential boiling off of the acetone molecules and the ensuing loss of free volume as the polymer becomes more glass-like. It is this second process that dominates, leading to the observed anomalous temperature dependence.

SUMMARY

In summary, the diffusion of printed dye into a spin-cast polymer film using a solvent-vapor-anneal is a promising method for the patterning of full-color polymer OLED displays. We have investigated the mechanism of this process by performing solvent-vapor-anneals at different polymer temperatures. These experiments indicate that dye diffusion decreases as the polymer temperature is increased, in contrast to a conventional thermal diffusion process. This trend can be understood by noting that the mechanism of diffusion enhancement is the absorption of the solvent vapor by the polymer, causing a decrease in polymer T_g that allows dramatically increased diffusion. As the polymer is heated, less solvent vapor is absorbed and the effect is diminished.

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