Fabrication and Characterization of Planar and Channel Polymer Waveguides. III. Compositional Distribution and Solute Loss in Polymer Thin Films

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ABSTRACT: For many microelectronic and optoelectronic applications, polymer thin films require the addition of small molecules. However, the thin-film geometry and associated processing techniques will influence the final morphology and compositional distribution of the constituents. It is therefore important that these be examined directly rather than inferred from bulk measurements. As an example system, the concentration and distribution of Disperse Red 1 (DR1) molecules in poly(methyl methacrylate) thin films were examined. Ultraviolet visibility spectroscopy and dynamic secondary ion mass spectrometry indicate that the composition of the molecules decreased dramatically with thermal treatment of the film. The sublimation of the chromophore was observed to occur at temperatures well below the melting point of the small molecule and the glass transition of the pure polymer; this solute loss manifested itself in changes in the glass transition temperature of the film. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2021–2024, 2002

Key words: PMMA; DR1; polymer thin films; compositional distribution; solute loss

INTRODUCTION

Thin polymer films containing small molecules are critical for many current and emerging technologies, such as photoresists,[1] electro-optic modulators,[2] light emitting diodes,[3] electrical conductors,[4] and adhesives. The thin-film geometry (with the associated amplified role of interfaces) and processing techniques will govern the final morphology and compositional distribution of the constituents. It is therefore important that these be examined directly rather than inferred from bulk measurements. Many recent efforts have concentrated on a fundamental understanding of the phase behavior and chain dynamics in thin films of homopolymers, block copolymers, and blends[5–11]; however, relatively little is understood about the influence of small molecules on the physical properties of organic thin films. The concentration and distribution of the small molecules as well as the relaxation behavior (e.g., glass transition temperature, residual stress, thermal expansion) of the polymer system will dictate the overall device performance, and therefore, understanding these critical factors are of technological importance as well as fundamental interest.

EXPERIMENTAL

The DR1 (2-[4-(4-nitrophenylazo)-*N*-ethyl-phenylamino]ethanol) was purchased from Aldrich and the atatic Poly(methyl methacrylate) (PMMA) was purchased from Scientific Polymer Products with a molecular weight of 130,000 g/mol. Films were spin coated from 2 to 5 wt % cyclopentanone solutions onto glass slides for ultraviolet visibility (UV–Vis) spectroscopy and dynamic secondary ion mass spectrometry (DSIMS) analysis. Electronic spectroscopy was performed by using a Hewlett–Packard 8453A photodiode array spectrophotometer. Spectra were acquired between 200 and 1100 nm. UV–Vis spectroscopy of DR1 in toluene was completed by using quartz cuvettes ranging in path size from 0.1 to 10 mm.

PMMA diluted with 10 wt % of the electro-optic (EO) chromophore Disperse Red 1 (DR1) was chosen
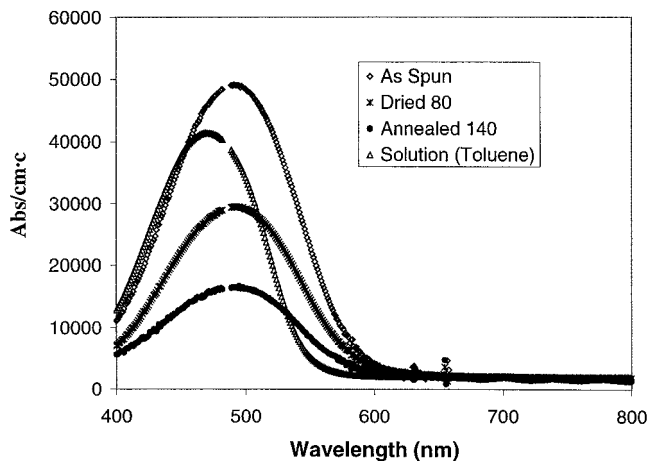
Figure 1 Normalized absorption of a PMMA film initially containing 10 wt % DR1 at various stages during processing. Spectra are normalized by film thickness (750 Å) which was measured by profilometry and initial DR1 concentration (0.35M). Spectra include DR1 in toluene (2.5 $\times$ 10^{-5}M) ($\triangle$) and the film immediately after spin coating ($\diamond$), after a 20-h drying step *in vacuo* at 80°C (*), and after a 2-h anneal at 140°C ($\bullet$).

as an initial system to examine the composition and distribution of small molecules in thin polymer films. DR1-PMMA films were extensively examined previously as a model EO polymer system and therefore the results herein have bearing on previously reported data in addition to the general behavior of polymer thin films containing small molecules. By use of UV–Vis spectroscopy and DSIMS, small molecule evaporation and segregation were quantified as functions of film processing.

RESULTS AND DISCUSSION

Figure 1 compares the normalized UV–Vis absorption of a film at various stages during processing from cyclopentanone (2–5 wt %). Specifically, the film was examined immediately after spinning, after a 20-h drying step under vacuum at 80°C, and after a 2-h anneal at 140°C. This represents the widely used procedure of removing solvent and annealing the film above glass transition temperature (T_g) to erase effects associated with process history. A spectrum of a 2.5 $\times$ 10^{-5}M solution of DR1 in toluene is also included for comparison. UV–Vis spectroscopy results of DR1 solutions in toluene ranging from 10^{-3} to 10^{-5}M yielded an extinction coefficient (ϵ) of 41,300 abs L/cm mol.

Figure 1 shows that, immediately after spinning, the film exhibits a maximum absorption λ_{max} at 487 nm, slightly red-shifted from the toluene solution spectrum. PMMA provides a more polar environment for DR1 than toluene, which stabilizes the ground state and thus causes the slight bathochromic shift relative to the absorption in solution.[12] The slightly larger

normalized absorption in the as-spun polymer compared to the toluene solution is associated with a slight dependence of ϵ on the local molecular environment and uncertainty in the molar concentration and path length of the thin film. The close correlation, though, indicates that the chromophore is not preferentially removed during the spin-coating process and that directly after spinning, the film contains $\sim$ 10 wt % DR1. However, a dramatic decrease in the normalized absorption, which is entirely associated with DR1, was observed after drying and again after annealing. Integrating under the absorption curves from 400 to 600 nm indicates that $\sim$ 57% of the chromophore was removed after the 80°C drying step, and an additional 43% of the remaining chromophore was subsequently removed during the annealing process. Only 25% of the initial chromophore concentration remains after annealing. In an analogous experiment where annealing at 140°C was conducted under vacuum, all the chromophore was removed. In accordance with the removal of chromophore ($\sim$ 6 wt % of the film) during the 80°C drying process, the thickness of the film ($\sim$ 75 nm) also decreases by $\sim$ 7% (determined by ellipsometry). Furthermore, dynamic ellipsometric measurements, wherein we monitor film thickness and refractive index as a function of temperature, revealed that the T_g of the film (determined by a change in dn/dT and dt/dT) increased from initially 82°C after the 80°C drying step to 103°C after the annealing.[13] This compares to T_g = 102°C for both dried and annealed pure PMMA films. Previous bulk measurements of the T_g of 10 wt % DR1/PMMA blends have been reported to vary from 75 to 90°C.[14]

The sublimation and degradation of chromophore are two possible explanations for the dramatic thermally induced reduction of the DR1 UV–Vis absorption in the PMMA film. Substantial degradation is not suspected because the position of the absorption peak is constant throughout the thermal treatment with no changes due to the presence of degradation products. Additionally, thermal gravimetric analysis studies show that DR1 does not degrade until 230°C in both air and helium. Potential sublimation of the chromophore is frequently ignored when processing at temperatures below its melting point (DR1: T_m = 160–162°C). However, the strong intermolecular interactions present in crystalline DR1 are absent when DR1 is dispersed in PMMA,[15] which results in a finite vapor pressure of DR1 above the film. The sublimation rate will be influenced by environmental conditions above the films, such as vacuum or flowing gases. Increased molecular weight[16] of the guest molecule or secondary interactions that tether a small molecule to the polymer matrix, such as hydrogen-bonding, acid-base, or ionic, will mitigate this sublimation.
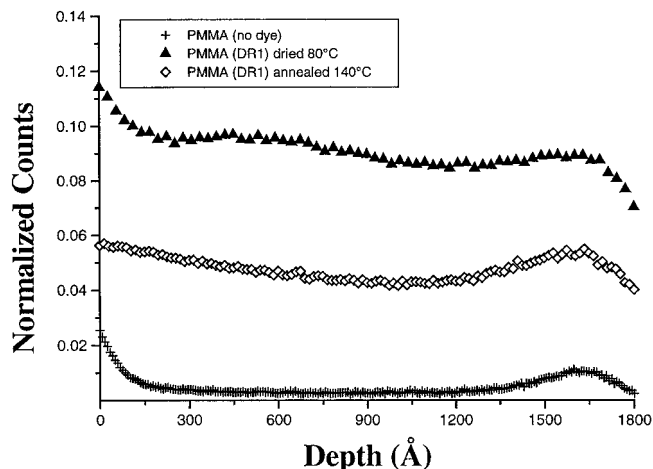
Figure 2 Normalized dynamic SIMS concentration profiles of negative mass 26 ions (mostly CN$^-$) with respect to negative mass 12 ions (mostly carbon) as a function of distance normal to the film surface for a PMMA film with no dye in it (+), a PMMA film with DR1 dried in vacuum at 80°C for 20 h (s), and a PMMA film with DR1 subsequently annealed at 140°C for 2 h (♦). The PMMA film was covered with a layer (~ 50 nm thick) of deuterated polystyrene floated on from the surface of water so that the SIMS damage profile would stabilize by the time the PMMA film surface was reached.

In general, the processing solutions described herein may be viewed as three-component systems (solvent—dye molecule—polymer). Within this framework, the relative affinity of the dye molecule for the polymer and solvent must be considered. In the extreme, the molecule may form an azeotrope with the solvent and be preferentially removed from the film in the original solvent drying step. Our initial experiments indicate that this occurs for polystyrene–DR1 films processed from cyclopentanone. Furthermore, the rapid removal of the solvent during film formation will act as a polarity gradient, facilitating preferential migration of the small molecule to a more favorable environment. Additionally, different surface energies for the components may favor segregation to the interfaces. Thus, not only the concentration but also the distribution of the constituents within the film will be highly dependent on processing history.

Figure 2 shows the normalized concentration of sputtered negative ions of mass 26 [primarily nitrile (CN$^-$) associated with the DR1] with respect to negative mass 12 ions [primarily carbon (C$^-$) proportional to the overall carbon concentration] as a function of depth normal to the film surface as determined by DSIMS. [Secondary ions of Si$^-$, CN$^-$, and C$^-$ were monitored as a function of time as a primary oxygen ion beam sputtered through a 10 wt % DR1/PMMA film. A discrete increase in the Si$^-$ signal and a corresponding decline in the C$^-$ and CN$^-$ identified the time at which the glass substrate was exposed. An independent measure of the film thickness used was

necessary to correlate the time to the sputtering depth (sputtering rate is assumed to be constant).] The depth profile for a PMMA film with no DR1 dye reflects a low concentration of mass 26 composite ions other than CN$^-$. For a film dried at 80°C, the DR1 is observed throughout the film with little evidence of strong segregation at either the glass substrate or the film surface. Upon annealing at 140°C, there is a substantial decrease in the normalized CN$^-$ signal over the entire thickness of the film. Integration of the two profiles gives a ratio of 0.56, which is in good agreement with the 43% loss in chromophore between the film dried at 80°C and the film after annealing at 140°C calculated from the UV–Vis spectroscopy measurements described above. The small concentration gradient across the film suggests that the diffusion of DR1 at 140°C is fast relative to the depletion of DR1 from the film surface by evaporation. An enhanced mass 26 signal near the glass substrate is seen but this may be associated with charging effects near the interface; thus, no firm conclusions can be drawn at this time about the existence of segregation at this interface.

In general, these results demonstrate that high temperature processing facilitates the loss of low molar-mass electroactive molecules in polymer films. Similar loss of low molar-mass constituents or preferential segregation of high molar-mass constituents in thin films of multicomponent systems such as photoresists,[17] polymer blends,[18] or block copolymers have been reported. Thus, evaporation and segregation should be critically examined when final processing temperatures approach 250°C in microelectronic applications. The dramatic loss of DR1, observed at temperatures well below the melting point of the pure chromophore, imply that even the low-temperature drying step used to remove processing solvent may reduce the chromophore concentration and subsequently the final nonlinearity of the DR1/PMMA films. Also, nonuniform distribution of the constituents normal to the film surface will greatly affect the field distribution in electrically active layers and propagating modes in optical waveguide structures. The importance of thin film polymer systems containing electroactive molecules motivates future efforts to combine spectroscopy, chemical analysis (DSIMS), and techniques to examine relaxations in thin films (variable temperature ellipsometry and reflectometry). Self-consistent field models and computer simulations to develop a detailed understanding of the enhanced role of interfaces on the thermodynamics and chain relaxations in these systems are also needed.

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