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Plasma polymerized hexamethyldisiloxane (HMDS) barrier layers

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Abstract

The number of applications employing polymeric optical materials is growing rapidly due to recent advances in telecommunications, display, and laser markets. For a number of these applications, organic dyes (chromophores) are added to the polymer host to add linear or nonlinear optical properties to the system. In homogeneous systems, dye diffusion is not an issue; however in multiple stacks of polymer films with different dye concentrations or in films with a spatially varying dye concentration, diffusion becomes important. We report here on initial studies to control the diffusion of the dye, zinc octabromylporpyhrin (ZnOBP), doped in poly(dimethylsiloxane) films, from diffusing into other layers in multiple stack systems. Plasma enhanced chemical vapor deposition (PECVD) was utilized to deposit thin films (60–240 nm) of hexamethyldisiloxane (HMDS) at the interface of two separate polymer layers, one with and one without ZnOBP. The diffusion of the chromophore to the outside surface of the undoped layer was examined with and without the plasma polymerized barrier layer. The thin but highly crosslinked interlayer is found to be an effective barrier to diffusion as measured using X-ray photoelectron spectroscopy to track bromine diffusion.

Keywords: Plasma polymerization; Diffusion; Poly(dimethylsiloxane)

1. Introduction

The ability to fabricate complex layered structures of polymer materials has numerous applications including mirrors, anti-reflection coatings, and nonlinear optical devices [1–3]. In a number of these applications, spatial grading of chromophore concentrations across the layers is necessary to optimize performance [4]. Approximation of a truly graded concentration gradient can be accomplished by stacking thin layers with different concentrations to approximate the original design. The choice of polymer is also important and is driven by good optical properties and compatibility with a wide range of chromophores. Siloxane polymers and elastomers are a candidate polymer class due to their high visible transparency, good mechanical properties, excellent processability, availability and their ease of modification.

In our attempt to make stacked designs with poly(dimethylsiloxane) (PDMS) films containing the chromophore zinc octabromylporpyhrin (ZnOBP), diffusion of the dye across interfaces occurred rapidly over the course of several days. This is in large part due to the use of a solvent, xylene, which solvates the chromophore in the PDMS material allowing for homogeneous, molecularly dispersed guest–host systems to be formed. However, diffusion of the dye across the interface between doped and undoped stacked layers is facilitated by this solvent processing. This diffusion was observed regardless of the local chemical structure of the PDMS network as varying crosslink densities were employed. To overcome this problem, plasma enhanced chemical vapor deposition (PECVD) of a thin film (60–240 nm) of crosslinked hexamethyldisiloxane (HMDS) between the PDMS layers was investigated as a possible diffusion barrier. Plasma polymerized HMDS is well suited for this application as the surface can be functionalized with Si-OH groups, capable of providing excellent wetting and adhesion upon application of a further room temperature vulcanized (RTV) silicone layer to build up optical stacks [5,6]. We report here on the chemical formulation of different PDMS stack structures, incorporation of chromophore, and the resulting diffusion properties from a variety

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of PECVD deposited interface films. We utilize polarizing optical microscopy and X-ray photoelectron spectroscopy to assess diffusion of ZnOBP between stacked layers.

2. Experimental

Dye-free crosslinked PDMS elastomeric networks were prepared from linear, hydroxy terminated PDMS, poly(diethoxysiloxane) (PDEOS), and dibutyltin dilaurate catalyst, which were purchased from United Chemicals. The manufacturer reports an average molecular weight of PDEOS of 610 g/mol. For PDMS, two polymers were used with average molecular weights of 1750 and 110,000 g/mol, resulting in two elastomers with different mechanical properties. The smaller molecular weight compound will result in a higher crosslink density in the final cured film. We refer to the two systems as A (higher crosslink density) and B (lower crosslink density). The chromophore, ZnOBP [7], was dissolved in xylene and then doped in the polymer precursor. The unit molecular structure of the reagents, catalyst, and dye are shown in Fig. 1.

The preparation of the two dye-free network structures is similar. For each system, a quantity of PDEOS was added to PDMS to give a 1:1 crosslink ratio (CR), defined, for our purposes, to be the ratio of hydroxy end groups on PDMS to the ethoxy functional groups on PDEOS. Dibutyltin dilaurate catalyst was added, with stirring, in a 10 wt% concentration. The samples were allowed to cure overnight at room temperature, resulting in a PDMS sample thickness of ca. 1 mm. The diameter of the films was approximately 25 mm. For the dye-doped polymer layer, the elastomer was prepared in the same manner as the dye-free layer with the following exceptions. A sample of PDMS (A or B) was mixed with the PDEOS in a 0.8:1 CR. ZnOBP (0.015 wt%) and xylene (6 wt% as solvent) were added to the mixture prior to addition of the catalyst. The approximate concentration of ZnOBP in the final cured films is 0.35 mmol. This mixture was then poured onto the fully cured system described above, and allowed to cure overnight, to create a stack without a barrier layer.

For the stacks with barrier layers, PECVD was used to deposit a thin film of crosslinked HMDS between the doped and undoped layers in the stack. To deposit this film, a fully cured, dye-free siloxane layer was placed into the RF plasma reactor. The flowing afterglow reactor has been described elsewhere in detail [8,9]. Argon (99.999%) was then flowed at a rate of 100–200 cc/min in a 10 cm diameter flow reactor at 1 Torr vacuum through a capacitively coupled, 13.56 MHz discharge with 10 W power. A calibrated flow of HMDS was added 20 cm downstream from the plasma (afterglow region). The plasma density in the afterglow was approximately $10^8\ \mathrm{cm}^{-3}$ and maintained an electron temperature equivalent to 1.5 eV. The HMDS polymer film was deposited at an average rate of 2 nm/min for 0.5, 1, 1.5, and 2.0 h, corresponding to thicknesses of 60, 120, 180, and 240 nm, respectively. A chemical structure for this layer, deposited under similar conditions, has been proposed [10]. The deposition of the HMDS was always accomplished on the dye-free layer.

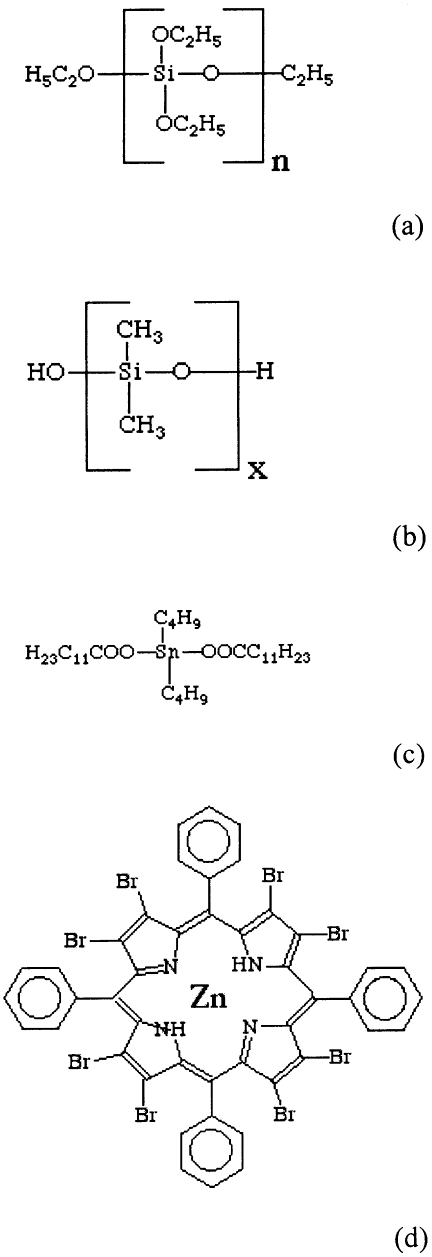

Fig. 1. Chemical structure of (a) poly(diethoxysiloxane), (b) poly(dimethylsiloxane), (c) dibutyltin dilaurate catalyst, and (d) zinc octabromylporphyrin.

Polarized optical microscopy (POM) was used to qualitatively examine the diffusion of the dye between the two layers, with and without the barrier layer. A piece was sliced out of the middle of the stack and imaged in cross-section. A Nikon Optiphot-POL microscope using white light was used to image the stacks.

Diffusion of the dye through a stack was also studied with XPS, by monitoring the bromine photoelectron signal from the surface of the undoped layer. Either zinc or bromine from ZnOBP could be used to monitor diffusion, and the Br 3d signal was selected as it has the highest sensitivity for detecting ZnOBP. The Br 3p and Zn 2p signals were used for confirmation. Measurements were also made on the surface of the doped layer as a reference. Small samples, approximately 5 mm square, were cut from the stacks, and examined in a Surface Science Instruments' M-Probe spectrometer. This instrument was equipped with a monochromatic Al X-ray source for photoelectron production. Samples were mounted on an aluminum holder with care to ensure that the surfaces to be examined were not touched in any manner, and then transferred through air into the spectrometer via a load-lock. The samples were not sputtered, and the pressure in the chamber during analysis was between 2 and 4×10^{-8} Torr. The overall surface composition was monitored by taking survey scans from 0 to 1100 eV binding energy, and the ZnOBP concentration was monitored by acquiring data at appropriate energy regions using the unscanned spectrometer mode. The spectrometer energy resolution was 1.5 eV for all data and the spectrometer covered an energy range of approximately 20 eV in the unscanned mode. The analysis area on the sample was approximately 400 μm × 1000 μm, with the depth of analysis being of the order of 10 nm.

3. Results and discussions

For stacks of compound A with no barrier layer, diffusion of the ZnOBP dye across the PDMS/PDMS interface can be seen visually as shown by POM in Fig. 2. The micrograph shows a cross-section of the stack perpendicular to the interface, with the region on the top right being the layer containing the dye while the region on the lower left initially contains no dye. The arrows mark the interface between the two PDMS layers. ZnOBP appears green in PDMS thereby making it an effective marker. The stack sat for approximately 48 h before the sample was prepped and imaged, and diffusion of the green ZnOBP dye across the interface can be clearly seen. The solvation of the undoped layer by the dye-doped mixture during deposition facilitates diffusion to occur. The use of xylene as a mutually common solvent enables a higher concentration of ZnOBP to be incorporated into the PDMS films. However, it also solvates the undoped PDMS layer, initially not containing dye. With no interface treatment, POM showed that the dye diffuses across into the non-doped layer as indicted in Fig. 2. After 1 week time period, the doped and undoped layers are visually indistinguishable.

As a comparison, lack of diffusion between stacks of A that were separated by a 180 nm barrier layer can be seen in Fig. 3. Fig. 3 is a cross-section of the two PDMS films with a plasma deposited HMDS barrier layer at the interface that has also sat for 48 h. On this time scale, the plasma deposited barrier layer has significantly limited ZnOBP diffusion as indicated by no green coloring in the undoped layer.

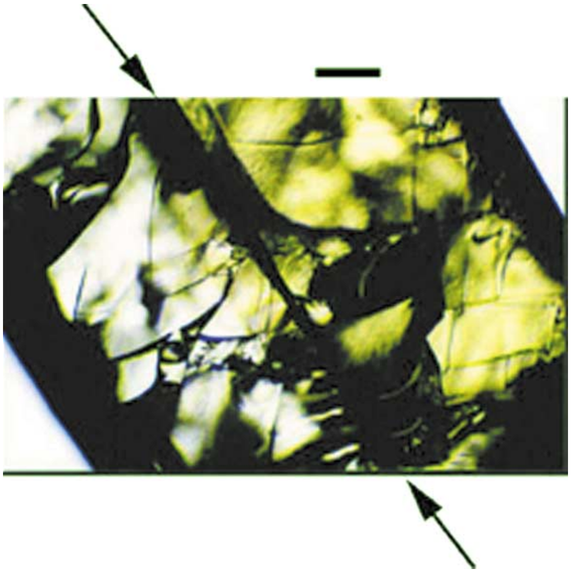

Fig. 2. Polarizing optical microscopy of two crosslinked polysiloxane layers, one containing chromophore (top right) and one initially containing no chromophore (bottom left). The arrows mark the interface between the two PDMS layers. No plasma-polymerized interface is present. The sample was photographed 48 h after processing. The scale bar corresponds to 250 μm.

An XPS survey scan from the surface of a ZnOBP doped layer is shown in Fig. 4. The Br 3d signal near 70 eV binding energy is shown more clearly in the inset. The Sn 3d signal in Fig. 4 is from the dibutyltin dilaurate catalyst. To

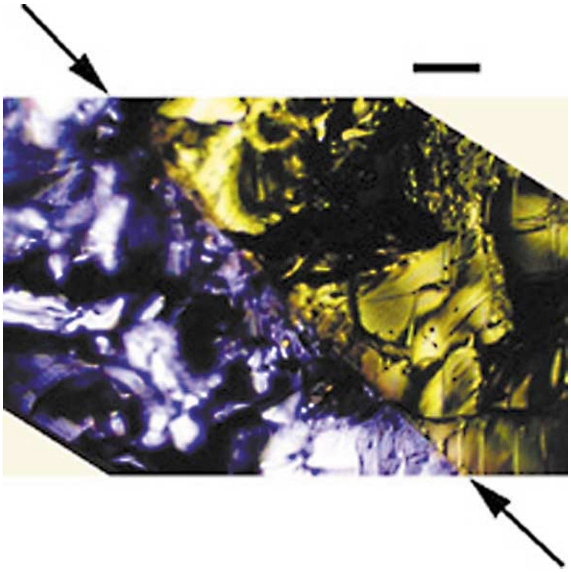

Fig. 3. Polarizing optical microscopy of two crosslinked polysiloxane layers, one containing chromophore (top right) and one containing no chromophore (bottom left). The arrows mark the interface between the two PDMS layers. A 180 nm plasma polymerized HMDS layer was deposited at the interface. The sample was photographed 48 h after processing. The scale bar corresponds to 250 μm.

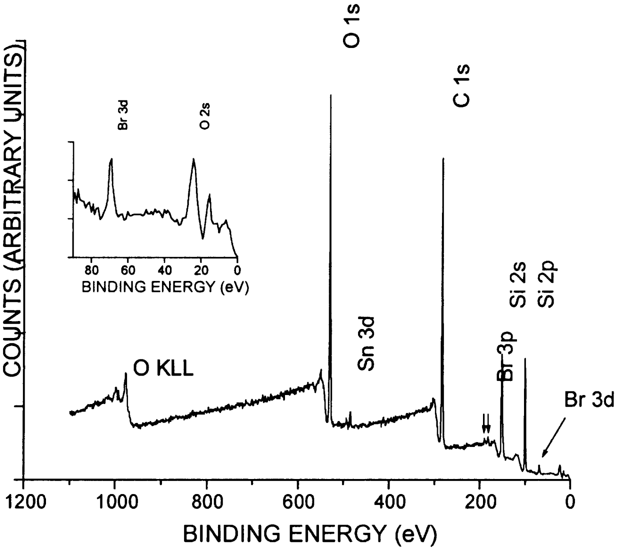

Fig. 4. XPS survey spectrum of chromophore-doped crosslinked polysiloxane with the characteristic XPS peaks labeled. The bromine 3d peak, occurring near 70 eV as indicated by an arrow, is shown enlarged in the inset. The spectrum took 10 min to acquire.

improve the detectability of Br, the spectral region for the Br 3d signal was acquired separately for 15 min, resulting in a Br detectability limit of 0.02 atomic%. When testing for diffusion of ZnOBP, the bottom side of the dye-free layer was chosen as the analysis surface. Since XPS is only sensitive to atoms present in the first few molecular layers, the presence of bromine on the surface of the undoped film indicates diffusion has occurred through the interface and through the entire thickness of the undoped layer. Fig. 5 shows the Br 3d XPS spectral regions obtained from the surfaces of dye-free layers from four PDMS A stacks, (a)–(e), and the surface of a dye-doped layer, (f), after 5 days. Fig. 5(a)–(d) were taken from stacks that had barrier layers that were 60, 120, 180, and 240 nm thick, respectively, and (e) was taken from a stack without a barrier layer. The lack of a Br 3d peak near 70 eV for the samples with barrier layers, (a)–(d), indicates that the barrier layers were successful in limiting diffusion. In contrast, a Br 3d peak was observed in the spectrum from the undoped surface of a stack without a barrier layer, (e), showing that diffusion of the dye through the undoped layer had occurred. For comparison, the spectrum from the surface of a doped layer is shown in (f). All four-thickness barrier layers were effective in limiting diffusion over 5 days.

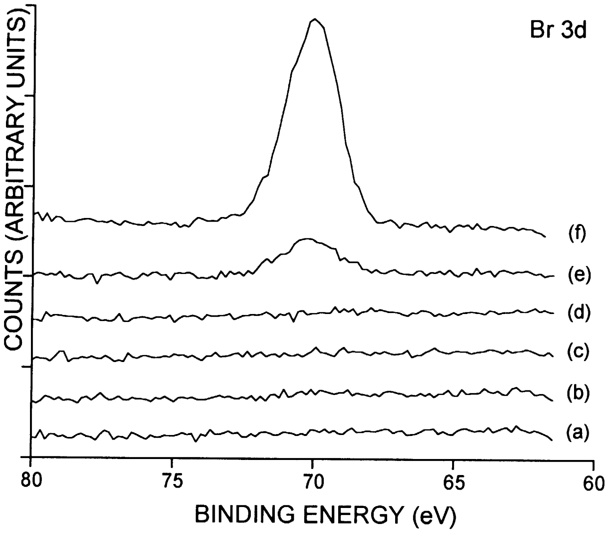

Fig. 5. Br 3d XPS spectra from the undoped layer surfaces of five undoped/doped stacks, (a)–(e), and from the surface of a doped layer as a reference, (f). (a), (b), (c), and (d) have a plasma polymerized HMDS layer deposited for 0.5, 1, 1.5, and 2.0 h between the undoped and doped layers, respectively, (e) has no HMDS barrier layer between the undoped and doped layers, (f) is a reference spectrum from the surface of a doped layer. All spectra were taken 5 days after the formation of the stacks and each spectrum took 15 min to acquire. The spectra have been offset for clarity.

Initial experiments on longer time scales also indicate that the barrier layer limits diffusion although not completely eliminating it. At three months time, both the 60 and 120 nm thick barrier layers allowed enough dye to diffuse between layers to exceed the detection limit of 0.02 at% bromine, whereas the 180 and 240 nm barrier layers did not. This longer-term data indicates that the thickness of the barrier layer is a key parameter in determining the longer-term effectiveness of completely stopping diffusion across the interface.

The XPS results also reveal a difference with chemical structure as the diffusion minimization obtained by films of PDMS A varied from PDMS B. The latter sample showed only a minimum reduction in diffusion with application of the barrier layer after 5 days time. The deposition of the crosslinked HMDS is therefore affected by the structure at the interface.

In conclusion, we have shown that the use of plasma enhanced chemical vapor deposition to deposit thin barrier layers of hexamethyldisiloxane is a possible methodology to limit or eliminate diffusion of chromophores across interfaces in optical stacks. The thickness of the barrier layer and the molecular architecture of the substrate both play a role in the diffusion reduction properties of the barrier layer. More extensive longer time scale studies are planned.

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