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Characterization of Crosslinked Electrooptic Polyimides

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ABSTRACT

The electrooptical properties of Ultradel® 9000D polyimides doped with DCM and DADC, a bis(carbazole) analog of DCM with improved thermal stability, are reported. Cure temperatures were restricted to 240 °C or less to minimize potential thermal degradation of these dyes. Low poling fields of 30 V/μm were used in these experiments and yielded r_{13} coefficients in the 0.1-0.8 pm/V range. Photothermal deflection measurements of dye-doped Ultradel 9000D samples showed low optical absorption losses in systems cured at 175 °C, but losses exceeded 20 dB/cm in samples cured at 300 °C.

1. INTRODUCTION

Ultradel 9000D polyimides are partially fluorinated aromatic polyimides, a family of polymers that have potential as the basis for integrated optoelectronic devices due to their good dielectric and optical properties, excellent thermal stabilities and compatibility with semiconductor processing conditions.¹ Semiconductor process compatibility requires component stabilities of 300 °C or higher for package assembly operations.

Single-mode optical waveguides based on these and related polymers have been fabricated.² When integrated to form optical multichip modules, such linear optical waveguides are proposed for use as high speed interconnects. In such designs, electrooptic polymer waveguides would be used to impress data on these lines. Polyimide matrices incorporating electrooptical dyes hold promise in these applications due to their potential ease of integration and resulting low cost.

We previously reported the use of aromatic donor-acceptor azole (oxazole, imidazole, thiazole) dyes with high thermal stability which were designed and synthesized for incorporation into Ultradel 9000D polyimide films.³ These dyes showed exceptional thermal stability, but absorbed at short wavelengths (< 400 nm) and had correspondingly low $\mu\beta$ values. For this study, the commercially available laser dye DCM and its derivative DADC⁴ were employed. While DCM lacks the exceptional thermal stability of the azole derivatives, DADC shows excellent thermal stability below 350 °C. Both of these dyes have hyperpolarizabilities sufficient for electrooptic experiments.

2. DYE AND POLYIMIDE STRUCTURE AND OPTICAL CHARACTERIZATION

2.1 Nonlinear optical dye structure and properties

An NLO dye with the ideal properties of high $\mu\beta$, high temperature stability (minimal decomposition at > 300 °C for 1 hour), low optical loss, and excellent solubility in the host matrix has not yet been reported -- though dyes with subsets of these characteristics are known. We previously reported the synthesis and properties of azole dyes that contain the relatively weak methoxy donor and cyano or sulfone acceptor groups (Figure 1). These dyes showed excellent thermal stability and were photobleachable. Their relatively short wavelength of absorption, combined with their relatively low oscillator strengths for the lowest energy transition yielded a small hyperpolarizability -- about 4 times that of p-NA.⁵

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As this study emphasized the evaluation of Ultradel 9000D as a host for electrooptical dyes, chromophores with high $\mu\beta$ but lower thermal stabilities were chosen as polymer dopants. DCM and DADC (Figure 1) are based on the same amino styrene/dicyanovinyl merocyanine. Whereas DCM sublimes at temperatures above 225 °C significantly below the recommended curing temperature of Ultradel 9000D (300 °C), DADC has higher thermal stability and lower volatility. Lower cure temperatures required to minimize DCM sublimation were expected to limit the temporal stability of the poled polymer.

Figure 1. Dyes used in this study included DCM, DADC, and two azole based dyes.

2.2 Ultradel 9000D polyimide structure and properties

The polymer matrix used in this work was a highly fluorinated preimidized polyimide (Figure 2) engineered for optical waveguide and coatings applications.¹ Copolymerization of low concentrations of a photosensitizer and an alkylated cross-linking group into the polymer backbone provided a photocrosslinkable polymer. The synthesis, sample preparation, and characterization of the base polymer were described previously.² Optical losses in this polymer, measured by photothermal deflection spectroscopy (PDS) and waveguide loss spectroscopy (WLS) were shown to be approximately 0.3 dB/cm at 1.14 eV, with only slightly higher losses at 1.5 eV (830 nm).³ Such absorptive losses are acceptable for waveguide devices as long as the dye dopant does not add more than 0.5 dB/cm of loss to the guides.⁶

Figure 2. Structure of Ultradel 9000D photosensitive polyimides. R = alkylated photocrosslinking group. (Exposure energies required for crosslinking are 100-300 mJ/cm².)

3. CHARACTERIZATION OF DYE-DOPED POLYIMIDE FILMS

Coatings for optical loss and refractive index measurements were prepared by spin-coating γ -butyrolactone (GBL) solutions of neat or chromophore-doped polyimide onto silicon wafers or thermally oxidized silicon wafers. Coatings for photothermal deflection spectroscopy were spun onto thin Infrasil quartz substrates. All substrates were pretreated with a silane-based adhesion promoter. Sample thickness varied from 2 to 20 μm as a function of percentage solids and spinner speed.

3.1 Photothermal deflection spectrometry of dye-doped Ultradel 9000D films

The PDS data for pure and five dye-doped polyimide films are shown in Figure 3. Films of Ultradel 9000D, 17% DADC and two oxazole dyes were cured at 300 °C. The 17% DCM- and 17% DADC-doped samples were cured at 175 °C for 30 minutes (above 225 °C significant DCM sublimation occurs). The infrared C-H overtone and combination bands for all five dye-doped samples overlapped, indicating that the samples are free of gross contamination that might offset the curves.

In every doped sample UV absorptions tail into the near infrared and add significantly to the absorptive optical loss near 830 nm. This tail may arise from different effects. A recent study of oxazole dyes has demonstrated that absorptive losses are probably not due to dye-matrix interactions.⁷ Thus, in the oxazole dye samples, tailing from these dyes that normally absorb near 370 nm may be due to phase separation into polymer-rich and dye-rich regions. The strong coupling between the dyes could lead to significantly broader absorption and tailing into the infrared. The optical loss of the DCM-doped sample drops off comparatively rapidly despite both a significantly higher absorption coefficient and longer absorption maximum wavelength. It is not possible to conclude that phase separation -- or some other factor(s) -- contributes to the residual losses in this sample.

The greatly increased losses observed in the DADC sample cured at 300 °C relative to that cured at 175 °C are indicative of phase separation, decomposition, or both. Optical losses measured by waveguide loss spectroscopy on similar samples cured at 175 °C show much lower losses, which suggests partial decomposition of the dye in the polyimide at the higher cure temperature. The cure conditions employed were nominally under ppm levels of oxygen; nevertheless, further efforts to minimize possible oxidative degradation of this and other dyes are suggested by this data.

Figure 3. PDS spectra of pure and doped Ultradel 9000D films. Ultradel 9000D, Oxazole and 17% DADC samples were cured at 300 °C. 17% DCM and 17% DADC samples were cured at 175 °C for 30 minutes. These samples were unpoled. Multiplication of absorption coefficients by a factor of 4.3 yields losses in dB/cm.

3.2 Electrical and thermal properties of dye-doped polyimide films

Samples for dielectric spectroscopy were tested in a parallel plate geometry using aluminum electrodes. Chromophore-doped solutions were spin-coated to a thickness of 1-2 μm on aluminum coated silicon wafers then cured for 3 minutes at 100 °C, 30

minutes at 175 °C, and 60 minutes at 300 °C. The samples were prepared under yellow light to prevent photobleaching. Top electrodes were also sputtered aluminum, photolithographically defined to 1 mm². The samples were tested in air on a heated chuck from 30-360 °C.

The dielectric spectra for DADC-doped Ultradel 9000D are shown in Figure 4. The dielectric constants for both dye-doped samples were continuous from 25 to 350 °C indicating the absence of a glass transition below 350 °C. The dielectric constant for the DADC-doped sample increased modestly with chromophore concentration. These results were similar to those obtained with triaryloxazole-doped films reported previously.³

Figure 4. Dielectric constant of DADC-doped Ultradel 9000D measured at 1 MHz as a function of dye concentration and temperature.

Plots of the change in dielectric constant of dye-doped films as a function of dye loading are shown in Figure 5. This data strongly suggests that phase separation due to chromophore pairing or crystallization has occurred in at least the sulfone-oxazole doped film. Conversely, there is no evidence for phase separation in the DCM-doped sample at similarly high doping levels. There is insufficient data to determine phase separation in the other cases.

Figure 5. Change in dielectric constant with dye doping level.

4. POLED POLYMER SYSTEMS

4.1 Effect of poling temperature on r coefficient and short term decay

Dye-doped polyimide solutions were spin-coated onto indium tin oxide coated wafers and soft-cured at 175 °C for 30 min to remove solvent. Sputtered gold electrodes were deposited onto the polyimide film. The samples were raised to the poling temperature (T_p , 175-275 °C) over 15 min while poling fields of 30 V/ μ m were applied. After 15 minutes at T_p , the sample temperature was returned to ambient over 15 minutes with poling field applied throughout. Electrooptic coefficients were determined immediately after contact poling and at varying times afterward.

Electrooptic coefficients were measured in transmission mode using a Mach-Zehnder interferometer illuminated by the output of a continuous wave Ar-pumped Ti:Sapphire laser operating at 800 nm.⁸ Laser light was passed through a polarizer and chopped before entering the interferometer. The poled sample described above was placed in one arm of the interferometer and a glass wedge in the other. A 50 V, 5 kHz AC signal was applied to the sample. Interference fringes were detected with a lock-in amplifier at the voltage modulated frequency as the glass wedge was translated through the beam. A separate run measuring the amplitude of the interference fringes produced by the translation of the glass wedge allowed calculation of the in-plane electrooptic coefficient, r_{13} . The out-of-plane electrooptic coefficient, r_{33} , can be measured in this apparatus by changing the sample orientation with respect to the incoming laser beam.

Samples of 9% DADC-doped polyimide were poled at temperatures ranging from 175-275 °C. (Figure 7.) Initial r_{13} coefficients were similar (0.26 pm/V) at all poling temperatures. After thermal aging at 125 °C for 53 h, r_{13} coefficients were redetermined. Samples poled at higher temperatures showed no decay of r_{13} within experimental error. The r_{13} decay observed for the sample poled at 175 °C (42%) may be attributed to incomplete crosslinking of the polyimide host at this poling temperature.

Figure 7. Electrooptic coefficients for 9% DADC-doped polyimide as a function of poling temperature. r_{13} was determined immediately after contact poling. $r_{13}(\text{decay})$ was determined after aging at 125 °C for 53 h.

Similar measurements were carried out for samples containing 17% DCM-doped polyimide. The data in Figure 8 reveal higher r coefficients than were observed in the DADC-doped sample, as expected from the model of Singer, et al.⁹ Aging at 125 °C for 42 hours in air showed a significant drop in the r coefficient that may result from slow decomposition of DCM, depoling in this incompletely crosslinked matrix, sublimation loss of DCM from the polyimide host, or combinations of these factors.

Figure 8. Electrooptic coefficients for 17% DCM-doped polyimide as a function of poling temperature. r_{13} was determined immediately after contact poling. $r_{13}(\text{decay})$ was determined after aging at 125 °C for 42 h.

Short term aging studies show good stability of the electrooptic coefficient. A 9% DADC-doped polyimide showed excellent stability at 25 °C. Measured values of r_{13} corresponded surprisingly well (within 65-85%) with values of r_{33} calculated by the method of Singer, et al.,⁹ albeit the method does not completely account for processes below T_g . In both of the cases described above, clearly poling temperatures of greater than 200 °C are required to initiate the thermal crosslinking necessary for electrooptic stability. Further experiments are needed to fully examine electrooptic performance under proposed operational conditions.

5. CONCLUSIONS

The first electrooptic measurements on guest-host DCM- and DADC-Ultradel 9000D based materials have been made and show good temporal stability at room temperature. DADC-doped films poled above 200 °C show good r_{13} stability after two days at 125 °C. Substantial decreases in r_{13} for DCM-doped films are understood in terms of incomplete crosslinking at poling temperatures below 200 °C and by dye sublimation at poling temperatures above 225 °C. Experiments at higher poling fields and temperatures are needed to explore the electrooptical characteristics of these compositions under sustained elevated temperature conditions. Dyes with minimal decomposition at 300 °C for 1 hour (the preferred cure conditions for Ultradel 9000D) are needed to fully investigate the stability of the poled state because only under these conditions is the crosslinking reaction within the polymer driven to completion.

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