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Polyimide-based electrooptic materials

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ABSTRACT

The properties of new, high temperature optical materials based on dye-doped Ultradel® 9000D¹ polyimides are presented. Ultradel 9000D is a soluble, pre-imidized, fluorinated polymer with properties optimized for integrated optical applications. When thermally or photochemically cross-linked, it has a T_g approaching 400 °C and retains excellent optical transparency as measured by both waveguide loss spectroscopy (WLS) and photothermal deflection spectroscopy (PDS). The agreement between WLS and PDS data indicates that losses in polyimides are due to absorption, not scattering. Two thermally stable, donor-acceptor oxazole-based dyes were designed, synthesized, and doped into the polyimide at concentrations up to 25 percent by weight. The T_g of the doped polymers decreased from the neat polymer, but remained above 300 °C. The effects of doping on the dielectric constant, refractive index, and coefficient of thermal expansion of the polyimide are presented. The oxazoles also photobleach and thereby provide an additional means of photodefining waveguides in these materials.

1. INTRODUCTION

Ultradel 9000D polyimides are examples of aromatic polyimides, a family of polymers that have potential as the basis for integrated opto-electronic devices. As a group they offer good dielectric properties, excellent thermal stability and compatibility with semiconductor processing. Semiconductor compatibility requires stability at 300 °C or higher, temperatures which are used in package assembly operations such as die attach and soldering.

Single-mode optical waveguides based on these and related polymers have been fabricated previously.² When integrated to form optical multi-chip modules, such linear optical waveguides can be used for 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.

Aromatic donor-acceptor azole (oxazole, imidazole, thiazole) dyes with high thermal stability were designed and synthesized for incorporation into Ultradel 9000D polyimide films. These dyes were purified by column chromatography and their thermal stability was subsequently tested by a sealed tube differential scanning calorimetry technique. The most thermally stable dye candidates were mixed into polyimide solutions.

The properties of Ultradel polyimide spun-cast films heavily doped with thermally stable electrooptic dyes are presented here for the first time. The thermal, mechanical, optical and dielectric properties of these films were determined as a function of dye loading in order to investigate their suitability as electrooptic materials for integrated optoelectronic devices.

2. POLYIMIDE STRUCTURE AND OPTICAL CHARACTERIZATION

2.1 Ultradel 9000D polyimide structure

The polymer matrix used in this work is a highly fluorinated pre-imidized polyimide (Figure 1) engineered for optical waveguide and coatings applications.¹ Co-polymerization of low concentrations of a photosensitizer and an alkylated cross-linking group into the polymer backbone gave a photo crosslinkable polymer. The polyimide was prepared initially as a polyamic acid by mixing a stoichiometric ratio of aromatic diamines with aromatic tetracarboxylic acid dianhydrides and then

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chemically imidized. The resulting polyimide was precipitated in methanol, washed, dried and redissolved in a polar solvent such as γ -butyrolactone (GBL). The polyimide solutions were pressure filtered to 0.2 μm before use.

Coatings for optical loss and refractive index measurements were prepared by spin-coating neat or chromophore doped polyimide solutions on silicon wafers or thermally oxidized silicon wafers. Coatings for photothermal deflection spectroscopy were spun on thin infrasil quartz substrates. All substrates were pre-treated with a silane based adhesion promoter. Sample thickness varied from 2 to 20 μm as a function of percent solids and spinner speed.

Figure 1. Structure of Ultradel 9000D photosensitive polyimides. R = alkylated photocross-linking group. (Exposure energies required for cross-linking were 100-300 mJ/cm^2 .)

2.2 Photothermal deflection spectrometry (PDS) of Ultradel 9000D

The PDS measurements were carried out in the "transverse" mode³ using a highly stable, single mode, 633 nm He-Ne laser. The heating beam was provided by a 19 Hz chopped light from a short arc, high pressure Xe lamp passing through a single-pass grating monochromator with a band pass of ~ 12 nm. A partially masked Si photocell served as the probe beam detector, while the heating beam intensity was continuously monitored with a second Si photocell for normalization purposes. Spectrum normalization was accomplished by comparing the sample PDS response with that obtained with a reference sample fabricated by baking a flat black organic coating of low (4%) reflectivity on quartz substrates. Independent measurements of the reflectivity of the reference standard were made by standard methods. With proper vibration isolation of the PDS apparatus, the noise level for absorbance (αt) was ~ 3 ppm. The deflection medium employed was Fluorinert FC-75. In the data reduction it was assumed that the reflectivity of the polymers in FC-75 was not a function of photon energy. Because the optical indices of these polymers do not differ greatly from FC-75, the reflectivity at the polymer/liquid interface is small, and variations of this quantity with photon energy will not introduce serious errors in the calculation of the absorption coefficient. Sample thicknesses were measured with a Sloan Dektak at several positions in the region heated by the PDS beam.

The losses in pure Ultradel 9000D as a function of cure temperature (under nitrogen atmosphere) are shown in Figure 2. This graph shows absorption due to C-H overtone and combination bands at low energies and electronic transitions which tail from the ultraviolet. The minimum absorbance of approximately $7 \times 10^{-2} \text{ cm}^{-1}$ is at 1.14 eV (i.e. 0.30 dB/cm). Absorption losses generally increase with increasing cure temperature; however, the origin of the broad absorption at 1.6 eV in the 300 $^\circ\text{C}$ cured sample is unknown. The observed overall losses of 0.2-0.4 dB/cm are considered acceptable for passive waveguides operating in the near-IR.⁴

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Figure 2. Photothermal Deflection Spectra of Ultradel 9000D as a function of cure temperature.

2.3 Comparison of waveguide loss spectroscopy and photothermal deflection spectroscopy

Optical losses of Ultradel 4212 aromatic polyimide⁵ that was cured at 300 °C for two hours were determined by both waveguide loss spectroscopy (WLS) and PDS. These experiments were used previously to identify loss mechanisms in doped organic polymers.⁶ In WLS, light from a laser source is coupled into a TM mode of a polymer waveguide that has been deposited on a thick oxide coated silicon wafer. The scattered light produced by the guided streak was imaged with a video camera. A Cortex frame grabber converted the image to a two dimensional intensity profile. The total loss (absorption plus scattering) was determined from the slope of $\log(\text{intensity})$ versus propagation distance after averaging and background subtraction.

Figure 3. Combination of WLS and PDS data for Ultradel 4212.

The agreement between the PDS and WLS data in Figure 3 is excellent and indicates that losses in these films are due to absorption, not scattering. This is contrary to common assumptions about the losses in these materials.^{7,8} As the losses are intrinsic to the polymer, they represent a limit to the ultimate transparency of a waveguide.

3. NLO DYE DESIGN AND SYNTHESIS

3.1 Dye design considerations

Because the typical cure temperature for Ultradel 9000D is 300 °C, a conservative approach to dye design that maximizes thermal stability was chosen over other considerations for these initial dye-polyimide studies. Other important issues that must simultaneously be optimized include solubility, hyperpolarizability, and low attenuation in a waveguide.⁴ The approach described here was to attain maximum thermal stability through the use of linked aromatic rings. Such structures are closely related to known, thermally stable scintillators, but have donor-acceptor groups attached to opposite ends of the molecule (many of these new dyes are also fluorescent). The linear electronic spectra of candidate molecules were evaluated computationally using semi-empirical methods to guide syntheses toward dyes with the strongest oscillator strengths and red-shifted charge-transfer absorptions. Previous work at IBM⁹ suggested that dyes with the strongest donors (amines) and strongest acceptors (nitro or cyanovinyl groups) have significantly lower stability than those substituted with methoxy, sulfonyl and cyano groups. Similar trends were observed in this work.

3.2 Synthesis

All nine combinations of acceptors and azole ring elements shown in Figure 4 were synthesized as part of this work. Nitro substituted compounds decomposed at significantly lower temperatures than cyano- and sulfonyl- dyes. The thiazoles were often contaminated by small but significant amounts of difficultly separable oxazoles. Imidazoles showed significantly lower solubility than the analogous oxazoles and thiazoles, attributable to hydrogen bonding interactions, and also were not further examined. This process of elimination of candidate dyes led to the ultimate selection of cyano- and sulfonyl- substituted oxazoles as the baseline dyes for incorporation into Ultradel 9000D (Physical data for the compounds are listed in Table 1).

Figure 4. Donor-acceptor azole dyes synthesized for this work.

Triaryl oxazoles and thiazoles were prepared via acid catalyzed condensation of 4,4'-dimethoxybenzoin with amides or thiamides, respectively. For example, a 1,4-dioxane solution of 4-(methylsulfonyl)benzamide and 4,4'-dimethoxybenzoin was treated with sulfuric acid and heated at reflux for 18 hours to give 4,5-bis-(4-methoxyphenyl)-2-(4-methylsulfonylphenyl)oxazole. Imidazoles were prepared from 4,4'-dimethoxybenzil and an appropriate aldehyde in acetic acid with excess ammonium acetate. Spectroscopic data of the pure dyes were fully consistent with the assigned structures.

Of the nine dyes synthesized, the cyano- and sulfonyl-substituted oxazoles were chosen for further study on the basis of thermal stability and ease of purification. Thiazole derivatives are slightly red-shifted with respect to the oxazoles, but always contained small amounts of the corresponding oxazoles. When mixed with Ultradel 9000D in GBL, the sulfonyl oxazole dye led to solutions with increased viscosity. This property permitted the formulation of polymer-dye solutions with viscosities suitable for spin-casting at dye:polymer ratios of 25:75. In contrast, solutions containing the cyano dye were limited to 10:90 dye:polymer ratios.

Table 1. Selected Properties of Donor-Acceptor Azole Dyes

Compound	X	A	T _m (°C)	T _{dec} (°C)	λ _{max} (nm)
1a	NH	-CN	232	>400	362
1b	O	-CN	183	>400	362
1c	S	-CN	158	>400	369
2b	O	-NO ₂	207	364	397
2c	S	-NO ₂	140	342	396
3a	NH	-SO ₂ Me	233	>380	356
3b	O	-SO ₂ Me	210	>400	357
3c	S	-SO ₂ Me	182	>400	364

Absorption spectra were determined in ethyl acetate; thermal data were taken on a Perkin-Elmer DSC 7 using the sealed tube method of Whiting, L. F.; Labean, M. S. and Eadie, S. S. *Thermochemica Acta*, 136 (1988) 231-245.

4. CHARACTERIZATION OF DYE-DOPED POLYIMIDE FILMS

4.1 Thermal, mechanical, and dielectric properties of dye-doped polyimide films

Samples for thermal mechanical analysis (TMA) and dynamic mechanical analysis (DMA) were prepared by casting solutions of the chromophore doped polyimide in GBL on glass plates and curing in a nitrogen purged oven for 10 minutes at 100 °C, 30 minutes at 175 °C, and 60 minutes at 300 °C. The resulting films were approximately 50 μm thick and were removed from the glass by soaking the glass plates in water for several hours. No phase separation or crystallization of chromophores was observed. Undoped polyimide films were used as control samples.

TMA films were run from 25 - 400 °C on a Mettler 40 thermomechanical analyzer in the tension mode. The neat (undoped) polyimide film expands linearly at a rate of approximately 23 ppm/°C up to 300 °C and then begins to contract from 300 to 400 °C. The contraction is a result of annealing and thermally initiated cross-linking and is typical for polyimide films. The coefficient of linear thermal expansion (in ppm/°C) for the cyano and sulfonyl chromophore doped films increases only slightly up to 300 °C. As in the undoped samples, the temperature region from 300-400 °C is obscured due to film contraction from thermal annealing.

Films for DMA were tested on a DuPont 990 Dynamic Mechanical Analyzer in the tensile mode. Test conditions were 0-500 °C, 2 °C/min heating rate, 1 Hz oscillation frequency. The glass transition temperatures, *T_g*, of the doped and undoped samples were determined by the onset method (noting the initial drop in modulus, *E'*) and also by the midpoint method (tan delta). Addition of the chromophore decreased the *T_g* from 390 °C in the undoped sample to 310 °C for the highest loading, 25 weight-% doped sulfonyl dye sample (Figure 5). Plasticization of the polyimide host by chromophore dopants has been previously reported.^{9,10} However, in this case the choice of a high *T_g* pre-imidized polyimide host resulted in a doped polymer (*T_g* 310 °C) which is acceptable for most device applications.

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, curing for 3 minutes at 100 °C, 30 minutes at 175 °C, and 60 minutes at 300 °C. The samples were prepared under yellow lights 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 30-310 °C.

Figure 5. T_g of Ultradel 9000D as a function of sulfonfyl dye concentration prior to deposition and curing. (Approximately 82% of the dye loading remained after cure.)

The dielectric spectra are shown in Figure 6. The dielectric constant of all the samples is continuous from 100 to 310 °C. Consistent with the DMA results, this indicates the absence of a glass transition below 310 °C. The dielectric constant increases with chromophore concentration for the cyano dye doped up to 10 weight-%. For the sulfonfyl dye, the dielectric constant decreases at the 25 weight-% dopant level. The decrease in dielectric constant indicates dipole-dipole cancellation due to pairing of the methyl sulfonyl chromophores and may indicate a saturation limit for this system. (The increase in dielectric constant observed in all the samples below 100 °C is a result of moisture absorption of the thin films in an ambient, 40-50 % RH environment and is unrelated to chromophore doping).

Figure 6. Dielectric constant of Ultradel 9000D measured at 1 MHz as a function of dye concentration and temperature.

4.2 Refractive indices of dye-doped Ultradel 9000D

Refractive indices for the doped and undoped polymer coatings were made using a Metricon PC-2000 prism coupler modified with a He-Ne (633nm) and Amoco YAG Microlaser (1064nm). In plane (nTE) and out of plane (nTM) refractive indices were determined by using a polarizer to orient the light. The results of these measurements as a function of sulfonyl dye concentration are shown in Figure 7. Since the refractive index is cure temperature dependent, all the samples were cured for 1 hour at 300 °C. Some of the samples were exposed to UV light (i-line) on a Karl Suss mask aligner at exposure energies of 300 mJ/cm² as a test for photobleaching. The observed photobleaching is consistent with photochemical oxidation of the oxazoles.¹¹ The refractive index change was approximately 0.005 which is adequate for single mode waveguide patterning.

Figure 7. Refractive indices of thin films of dye-doped Ultradel 9000D.

The refractive index increases with chromophore concentration and reaches a saturation limit above 20 weight-% loading. Both the cyano and sulfonyl chromophore photobleach at these exposure energies as shown by the lower refractive index of the UV exposed samples.

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

The PDS data for undoped and two dye doped polyimide films cured at 300 °C are shown in Figure 8. The infrared C-H overtone and combination bands for all three samples overlap, indicating that the three samples are free of gross contamination which might offset the curves. The UV absorption tail for the doped samples shows a significant increase over the undoped samples such that the minimum absorption in the undoped samples occurs near 1.0 eV, rather than near 1.14 eV. The minimum absorption also increases from approximately 0.3 dB/cm to nearly 0.9 dB/cm at 1.2 eV in the case of the 10% cyano-dye doped material and nearly 1.5 eV in the case of the 15% sulfonyl-dye doped material.

The origin of the increased UV absorption may be due to several factors. Thermally unstable impurities or dye decomposition could give rise to such low energy absorption. Dye aggregation that gives rise to new transitions is also possible; however, aggregates were not observed by optical microscopy. Weak charge transfer interactions between dye molecules at these very high concentrations, or between the polymeric host and the dyes could also give rise to broad low energy absorption. The origin of this absorption is important as optical losses at a given wavelength in the near-IR are likely to increase with red-shifted dyes. As optical attenuations of <2 dB/cm are required for many devices, such absorption losses may drive the wavelength at which organic electrooptical devices operate.

Figure 8. PDS of doped and undoped Ultradel 9000D cured at 300 °C for one hour.

5. CONCLUSIONS

Absorption losses in Ultradel 4212 have been shown to arise from intrinsic absorption of the polyimide and are not due to extrinsic scattering loss. In the new fluorinated Ultradel 9000D pre-imidized, photosensitive polymers, these losses are in the 0.2-0.4 dB/cm range in the near-IR for films cured at 300 °C. These loss measurements show that high temperature polyimides are suitable for integrated optical interconnects.

A thermally stable sulfonyl oxazole dye has been doped at 25 weight-% into Ultradel 9000D films and the resulting amorphous materials have been characterized. The T_g of the polymer drops from near 400 °C in the pure polymer to 310 °C in the most heavily doped samples, and this T_g is believed to be adequate for long term stability. Optical losses increase with increasing dye concentration. Although optical attenuations are within acceptable limits, a better understanding of the origin of these losses is required as new dyes with lower energy charge transfer absorptions are likely to lead to significant losses near 800 nm.

6. ACKNOWLEDGMENTS

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7. REFERENCES

1. Amoco Chemicals *Ultradel 9000D Product Bulletin*.
2. A. J. Beuhler, D. A. Wargowski, T. C. Kowalczyk, and K. D. Singer, *Proc. SPIE*, 1849, 92, 1993.
3. W. B. Jackson, N. M. Amer, A. C. Boccara, and D. Fournier, *Appl. Opt.* 20, 1333, 1981.
4. For a discussion of the requirements on α , r , β and $\chi^{(2)}$ required for device applications, see R. Lytel et al., this volume.
5. Amoco Chemicals *Ultradel 4212 Product Bulletin*.
6. A. Skumanich, M. Jurich, J. D. Swalen, *Appl. Phys. Lett.*, 62(5), 446, 1993.
7. R. Reuter, H. Franke, C. Feger, *Appl. Opt.* 27(21), 4565, 1988.
8. H. Franke, *Polymers for Lightwave and Integrated Optics*, pp. 207-230, Marcel Dekkar, New York, 1992.
9. R. D. Miller, K. H. Betterton, V. Y. Lee, T. J. Matray, C. R. Moylan, C. Nguyen, R. J. Twieg, and C. J. Walsh, presented at the Materials Research Society Symposium on "Organic Materials for Nonlinear Optical Applications", San Francisco, CA, April 1993.
10. S. Ermer, J. S. Valley, R. Lytel, G. F. Lipscomb, T. V. Van Eck, D. G. Garton, *Appl. Phys. Lett.* 60, 160, 1992.
11. H. H. Wasserman, F. J. Vinick, and Y. C. Chang, *J. Am. Chem. Soc.* 94, 7180, (1972); K. Ichimura, T. Ikeda and H. Ito, *Makromol. Chem. Rapid Commun.*, 13, 415, (1992).

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