

polymer papers

Emission mechanism in polyimide

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The fluorescence properties of pyromellitic dianhydride–oxydianiline (PDMA–ODA) polyimide are described. The quantum efficiency of fluorescence following excitation at 290 nm is measured to be 10^{-6} . The spectroscopically parametrized (complete neglect of differential overlap) CNDO/S3 model is used to provide a quantitative description of the emission spectrum, and to make some preliminary conclusions about the mechanism responsible for laser etching of polyimides.

(Keywords: polyimide; polymer fluorescence; laser ablation)

INTRODUCTION

Polyimides are a technologically important class of materials that, because of their superior thermal and mechanical properties and low dielectric constants, have found wide application in the electronics industry¹. In addition, there has been considerable interest recently in the laser ablation of polymeric materials^{2,3}. It has been shown by Srinivasan² and others³ that, following the absorption of u.v. laser radiation, several polymers, including polyimide, can be etched with well defined features. This process has many potential applications in microelectronics and electronic packing technologies⁴. While various studies have been carried out to characterize the process and to understand its mechanism, they have focused on studying the volatile and non-volatile etch products^{5,6}. From observations on the energy distributions of the volatile products, it has been inferred that a photochemical process is responsible for the characteristically 'clean' etching behaviour⁶.

There has been very little work, however, on the photophysical properties of the polymers themselves. As with any material that is illuminated with light, an absorbed photon promotes a molecule from the ground state to an excited (usually singlet) state. The molecule can then undergo any one of the following processes⁷:

(i) It can relax back down to the ground state by emitting a photon either directly (fluorescence) or via a triplet state (phosphorescence).

(ii) It can relax back down to the ground state without emitting a photon, in which case the excess energy is converted into heat (i.e. vibrations).

(iii) It can undergo dissociation if the excited state is a repulsive state.

(iv) It can absorb another photon and go to a higher excited state following which any of the above processes can take place either alone or in the appropriate allowed combinations. For this to happen, the molecules must have a long excited-state lifetime and/or a large excited-state absorption cross-section.

It is clear from this discussion that, to understand fully the laser etching process in polyimides, their photophysical properties, namely absorption, emission and excited-state lifetimes, must be characterized. For instance, if the lifetime of the first excited state of a polymer is long, then the probability of photochemical etching via a two-step absorption from the ground state to a dissociating state via the first excited state is increased.

The aim of this paper is to extend our previous work on the characterization of the photophysical properties of polyimide⁸. In that paper, the electronic structures of pyromellitic dianhydride–oxydianiline (PDMA–ODA) polyimide and several model compounds were investigated. The u.v. absorption spectra were experimentally determined and the (complete neglect of differential overlap) CNDO/S3 model was used to provide a quantitative description of the experimental data. In this paper we describe measurements of the emission spectrum of PDMA–ODA polyimide (Dupont Kapton[®]) following excitation at 290 nm. The emission spectrum, the polarization behaviour of the emission and its quantum efficiency are measured. The 290 nm wavelength was chosen since it falls in the same absorption band as the 308 nm output of the XeCl excimer laser. Finally, CNDO/S3 model calculations are used to provide a theoretical understanding of the experimental data, and to provide some insight into the laser etching mechanism.

METHODOLOGY

Experimental

The experimental apparatus is shown in *Figure 1*. A Lumonics 860-TE XeCl excimer laser is used to pump a narrow-band Lambda Physik 2002FL dye laser. Solutions of rhodamine 6G in methanol at concentrations of 1.2 and 0.4 g l⁻¹ were used in the oscillator/preamplifier and amplifier respectively. We excite polyimide at its first absorption peaks at 290 nm^{8,9}. This is accomplished by tuning the rhodamine dye laser to 580 nm, where it lases

efficiently, and frequency-doubling the output in a KDP crystal (Inrad Auto Tracker II). The output of the doubling crystal, which consists of the fundamental (580 nm) and second harmonic radiation (290 nm), is then frequency-separated in a dispersing prism and the 290 nm radiation is directed onto the sample with a 90° turning prism and a mirror. The dye laser pulse has an energy of 2 mJ and the energy of the 290 nm (frequency-doubled) pulse is 40 μ J. The latter is incident on an area of 0.02 cm², leading to a fluence of 2 mJ cm⁻², which is below the etching threshold (50 mJ cm⁻²) for polyimide at 308 nm, the nearest wavelength for which data are available⁶.

The fluorescence of the sample is collected with a 5 cm focal length, *f*/1.0 lens and focused onto the input slit of a 0.1 m double-pass monochromator (Instruments S.A. model DH-10). Slits 1 mm wide are used at the entrance, exit and intermediate positions, resulting in a 6 nm wavelength resolution. The fluorescence is dispersed and detected with a photomultiplier (PMT). The laser is operated at a repetition rate of 10 Hz to avoid sample heating and the signal detected by the PMT is averaged using a gated integrator (Kinetic Systems Camac). The data collection is computer-controlled.

Theoretical

The CNDO/S3 model was developed by Lipari and Duke for the computation of electronic spectra¹⁰. The model is parametrized by optimizing the overlap integrals and the orbital exponents to give the best fit to the spectra of some representative compounds. The parameters used in this study are shown in Table 1 and are taken from previous studies⁸. A complete mathematical description of the model¹⁰ and its applications¹¹ are given elsewhere. Figure 2 shows the model compound and the geometric parameters used in the CNDO/S3 computations.

EXPERIMENTAL RESULTS

Figure 3 shows the measured fluorescence from a 12.5 μ m thick film of polyimide (Kapton). The fluorescence begins

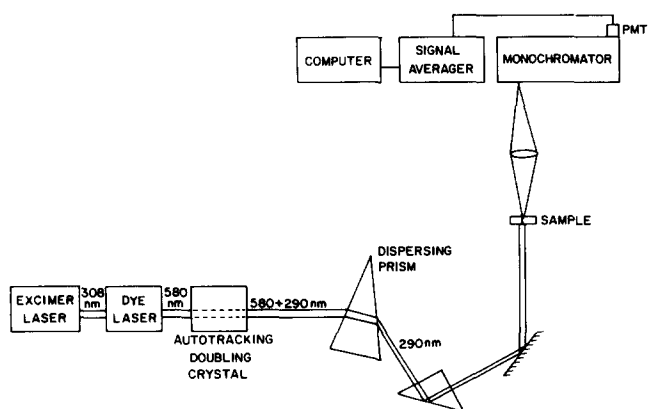


Figure 1 Schematic diagram of the experimental apparatus

at approximately 500 nm and extends past 800 nm, the limit of our spectrometer, with a maximum at approximately 600 nm. To be certain that the weak emission observed was not an artifact of the measurement system, the Kapton sample was substituted with samples of quartz, milk glass and a metal mesh scatterer, all of which produced distinctly different emissions at the same detection level. Moreover, a spin-coated and cured 2300 Å thick film of polyimide (PMDA-ODA) made with zone-refined starting materials produced an emission

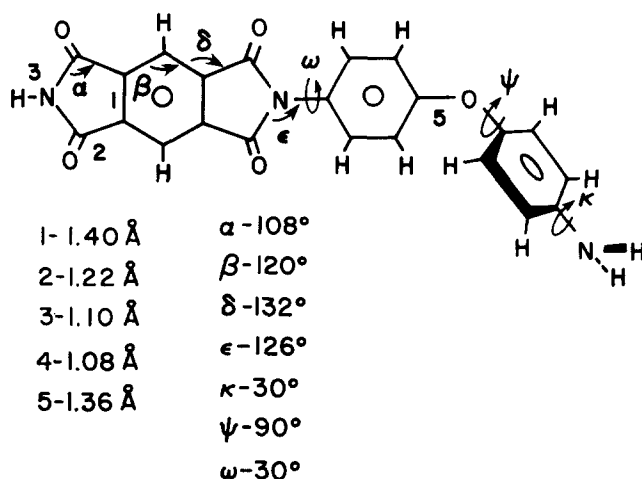


Figure 2 Model PMDA-ODA compound and geometric parameters used in the CNDO/S3 configuration-interaction (CI) computations

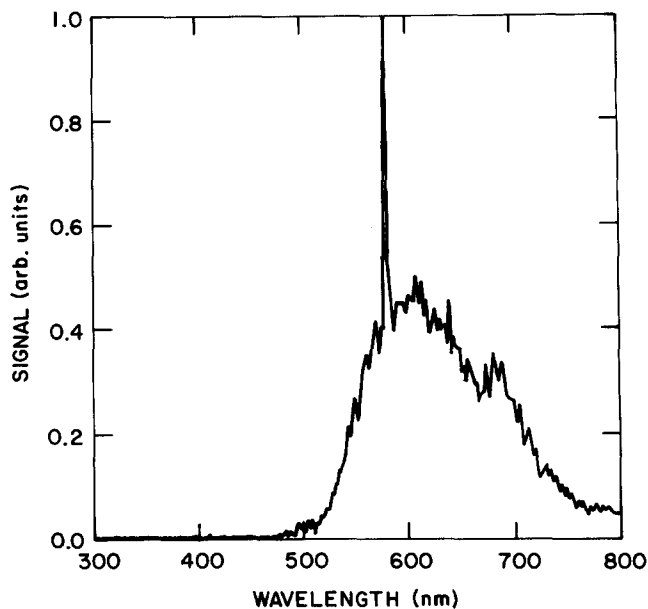


Figure 3 Observed emission spectrum for the 12.5 μ m thick film of Dupont Kapton. The spike at 580 nm is the scattered second-order incident radiation at 290 nm

Table 1 Parameters used in the CNDO/S3 model

Atom	I_s (eV)	I_p (eV)	β_s (eV)	β_p (eV)	γ (eV)	ζ_s (Å ⁻¹)	ζ_p (Å ⁻¹)
H	13.60	—	10	—	12.85	2.33	—
C(sp ²)	21.34	11.54	20	17	10.63	3.78	3.78
C(sp ³)	21.34	11.54	20	17	10.63	3.07	3.07
N	27.51	14.34	25	20	12.37	3.22	3.22
O	35.50	17.91	31	26	13.10	4.32	4.32

spectrum identical to that observed for the Kapton film. Because the fluorescence of the Kapton was very weak, the measurements were made in transmission mode to facilitate alignment. Since the fluorescence of the 2300 Å film of PMDA-ODA and the 12.5 μm thick film of Kapton were the same spectrally and in intensity, and PMDA-ODA has negligible absorption in the 500–800 nm wavelength range¹², we believe that the measurements made in the transmission mode are a true representation of the fluorescence spectrum of polyimide. In addition, the spectrum is essentially identical to the emission spectrum reported by Wachsman and Frank¹³, following excitation at the low-intensity absorption at 380 nm. The fact that excitation at either of these wavelengths produces identical emission spectra will be addressed in a following section.

Phosphorescence was searched for by delaying the gate pulse past the main fluorescence peak and averaging over a longer time at the same PMT voltage. No signal was observed in the wavelength range of 300–800 nm.

The quantum efficiency of the fluorescence was measured using *p*-terphenyl dissolved in cyclohexane as a standard. Since *p*-terphenyl has a strong absorption peak at 275 nm and a known quantum efficiency¹⁴, the emission from a dilute solution (2×10^{-6} M) in a 1 mm thick cuvette was measured, and values of the integrated fluorescence from both polyimide and *p*-terphenyl were compared at the same detection sensitivity. The measured fluorescence spectra of the dilute *p*-terphenyl solution and polyimide (with the peak due to incident radiation subtracted) are shown in Figure 4. The quantum efficiency of fluorescence of polyimide was calculated to be 9.7×10^{-7} .

The quantum efficiency is defined as:

$$\eta_k = A_k / (A_k + R_k) \quad (1)$$

and gives the ratio of the spontaneous transition (fluorescence) rate (A_k) to the total deactivation rate, which includes the radiationless processes (R_k)¹⁵. Hence, the extremely low value determined for polyimide suggests that the deactivation processes that dominate the emission mechanism in polyimide are radiationless, and implies

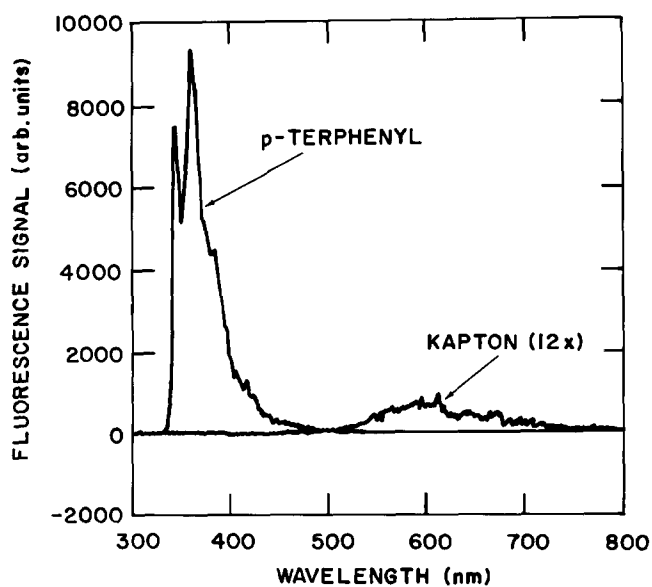


Figure 4 Observed emission spectra for *p*-terphenyl and polyimide

Table 2 Measured and calculated optical absorption bands in PMDA-ODA polyimide (oscillator strengths are given in parentheses)

Experimental (eV)	CNDO/S3 ^a (eV)
3.3	3.05 (10^{-3})
4.4	3.91 (0.12)
	4.36 (0.15)
	4.57 (1.2)
	4.63 (0.18)
	5.05 (0.25)
5.9	5.73 (0.64)
	5.77 (0.47)
	5.88 (0.13)
	6.00 (0.58)
6.4	6.29 (0.66)
	6.30 (0.84)
	6.31 (0.24)
	6.45 (0.77)
	6.47 (0.35)

^a 8×8 configuration interaction

that emission occurs from a state other than that responsible for absorption.

The polarization behaviour of the emission was determined by inserting a Glan-Thompson polarizer at the spectrometer input and measuring the fluorescence spectrum parallel and perpendicular to the incident radiation. Measured this way, the two spectra had the same shape as the unpolarized spectrum but with different intensities. The degree of polarization, P , is given by:

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} = \frac{3 \cos^2 \alpha - 1}{\cos^2 \alpha + 3} \quad (2)$$

where I_{\parallel} and I_{\perp} are the integrated fluorescence intensities parallel and perpendicular to the input polarization, and α is the angle between the dipoles responsible for the absorption and emission. After accounting for the different collection efficiencies of the monochromator for parallel and perpendicularly polarized light, P is found to be ~ 0.2 ($\alpha \sim 41^\circ$), which implies that the dipole responsible for emission is not the same dipole responsible for the absorption at 290 nm, the wavelength at which the polyimide is pumped. This is consistent with observations regarding the low measured quantum efficiency.

Domains of crystallinity in thin-film polyimides have been observed¹⁶, which, if ordered, would affect the value of P . To determine this, emission spectra were taken with the sample in its initial and perpendicular orientations; no differences in either the shape or intensity of the spectrum were observed. Hence, the crystalline domains must be randomly oriented with respect to the incoming radiation, and therefore do not affect the degree of polarization.

MODEL CALCULATIONS

The results of the CNDO/S3 computation are listed in Table 2 and show that, while the first strong absorption ($f > 1$) occurs at ~ 4.4 eV (and is long-axis (x) polarized), the lowest-energy excited singlet state is at ~ 3.1 eV (and is short-axis (y) polarized), with a computed oscillator strength of 6×10^{-4} . This is consistent with the observed absorption spectrum of PMDA-ODA^{8,17}. The observed low-intensity absorption at 3.3 eV was initially thought

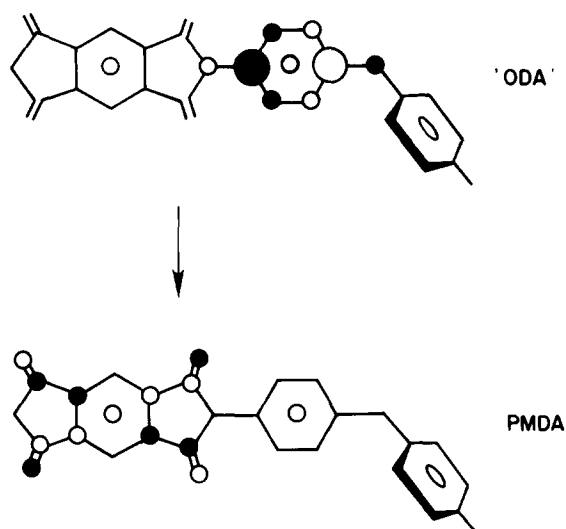


Figure 5 One-electron orbitals involved in the transition primarily responsible for the lowest-energy excited singlet state at 3.3 eV. Note that this is an intramolecular charge-transfer transition, from the diphenyl ether to the imide

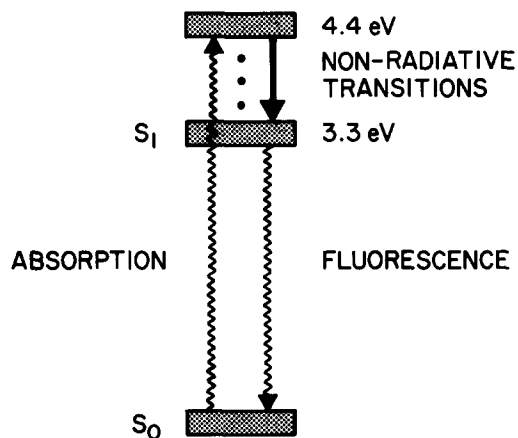


Figure 6 Schematic diagram of the emission mechanism for PMDA-ODA polyimide

to be intermolecular in origin¹⁸, but is now interpreted as an intramolecular charge-transfer transition^{13,17} with electron density shifting from the diphenyl ether moiety to the imide. *Figure 5* shows the one-electron orbital involved in this transition, and confirms this assignment¹⁹.

Based on these results, the following interpretations of the fluorescence process are proposed (and shown schematically in *Figure 6*). After excitation by the 290 nm (4.3 eV) radiation, the polymer undergoes a series of radiationless transitions down to the lowest excited state at 3.3 eV (3.1 eV from the computations). From this state the polymer fluoresces down to the ground state. The energy difference between the lowest excited singlet state and the observed fluorescence (600 nm or 2.1 eV), due to electron-phonon coupling, is not included in the model.

The low oscillator strength computed for the lowest excited singlet state is consistent with the low observed quantum efficiency for the fluorescence, and the different computed polarizations are consistent with observed degree of polarization. This interpretation also provides an explanation for the fact that identical emission spectra are observed following excitation at both 290 nm (4.3 eV) and 380 nm (3.3 eV).

LASER ETCHING OF POLYMERS

A primary result of this study is that only a miniscule fraction of the energy absorbed by polyimide at its first strong absorption peak is re-emitted. Since the fluence used was far below the etching threshold, this energy must be converted into heat (i.e. vibrations). This is compatible with the calorimetric measurements of Gorodetsky *et al.*²⁰. From this, we are led to the conclusion that the mechanism responsible for the etching of polyimide when it absorbs a XeCl excimer laser pulse at 308 nm must be thermal degradation, since 308 nm is within the first absorption peak. This is further supported by the fact that 4 eV is below the bond energies of most bonds found in this type of molecule (e.g. 4.8 eV for C-H bonds, 4.5 eV for C-N bonds, and 4.8 eV for C-O bonds in aromatic compounds). However, if the lifetime of the first excited state, which has not yet been determined, is long, then a two-step photodissociation is still possible. It is a general observation that long excited-state lifetimes are associated with materials that fluoresce strongly. Thus it is unlikely that such a two-step process is occurring with polyimide since the quantum efficiency of fluorescence is so small. Further experimental studies including determination of the lifetimes of these states are necessary before a more definite conclusion about the laser etching mechanism can be made.

SUMMARY

The fluorescence spectrum of PMDA-ODA polyimide following excitation at 290 nm has been presented along with the measured polarization and quantum efficiency. Model computations using the CNDO/S3 molecular model provided a quantitative description of the emission spectrum, and a complete interpretation of the emission process. Furthermore, this understanding has allowed for the preliminary conclusion to be made that a thermal mechanism is responsible for the laser etching of polyimides at the 308 nm wavelength of excimer lasers.

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DISCLAIMER

This work represents the views of the authors and not necessarily the official position of the United States Military Academy, the United States Army, or any other government agency. Work of the US government, not subject to copyright restrictions.

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