High-Gain Long-Lived Amplified Spontaneous Emission from Dye-Doped Fluorinated Polyimide Planar Waveguides

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Introduction

Development of organic waveguide lasers based on dye-doped polymers has attracted much attention over the last decade for their potential applications in integrated photonics.[1–23] These gain media assure wide wavelength tunability and high efficiency with potentially very low cost, which makes them very attractive as the basis for very compact and versatile laser systems. A major drawback of these devices is their limited operational lifetime due to dye degradation, and any realistic application passes for extending it.

It is known that improvement in polymer thermal conductivity reduces dye degradation and increases the device’s lifetime.[24,25] Thus, any progress in the development of polymeric materials which combines adequate optical properties with improved thermal resistance could result in significant improvements in the lasing performance of devices based on dye-doped organic waveguides.

In past decades usage of imide polymers has increased considerably, and a huge number of contributions, both technical and scientific, have been made in a wide variety of applications.[26–29] Aromatic polyimides have gained a prominent position among high performance polymers because of their excellent balance of properties, in particular the very favorable combination of mechanical, electrical, and thermal resistance. Increase in the demand and technological advances are fostering a growing interest in these special polymers, and research efforts are focusing on developing and modifying aromatic polyimides to accommodate their chemical composition to fulfill technical requirements.

Long-lived amplified spontaneous emission (ASE) action is demonstrated in waveguides based in transparent newly synthesized fluorinated polyimides (FPI) doped with laser dye Pyromethene 597. Relevant parameters to optimize the lasing performance of the guides are the polymer chain density and fluorine content. The guide with the higher fluorine content was the most stable, with the ASE emission remaining at 50% of its initial value after 40 000 pump pulses of $\approx 220 \text{ kW} \cdot \text{cm}^{-2}$ delivered at a repetition rate of 5 Hz. Net gains of up to 93 cm$^{-1}$ were obtained at a pump intensity of about 500 kW$\cdot$cm$^{-2}$ (34 $\mu$J pulse$^{-1}$).
Fluorine containing polyimides have proved to be specially suitable for these modern applications, and fluorine-containing dihydrides and diamines have provided new opportunities for chemical manipulation and development of new materials.\(^{[30,31]}\) Possibly the most important fluorine containing dihydride is hexafluoroisopropylidene diphthalic anhydride (6FDA) which exhibits a special potential to impart a low dielectric constant in polymers as well as outstanding solubility in organic media.\(^{[32,33]}\) Processing is very difficult for heterocyclic polymers, such as aromatic polyimides, due to the fact that they do not melt before decomposing and are virtually insoluble in organic solvents. Thus, the use of solubilizing monomers, such as 6FDA, is an attractive approach to develop novel polyimides. However, 6FDA and fluorinated diamines are very expensive reactants, and their utilization as condensation monomers is, therefore, limited to the development of materials for special applications.

Only some fluorinated polyimides (FPI) offer a balance of properties very favorable to be used as host materials for lasing chromophores, combining excellent thermal properties with good optical transparency at the wavelengths of interest, which is perhaps the most outstanding property for a polyimide in this application. Nevertheless, although various FPIs have already been used as passive\(^{[1,34]}\) and dye-doped active waveguides\(^{[32,35,36]}\) mostly in the infrared (IR) region, to the best of our knowledge there have been no previous studies on their photostability properties under laser irradiation.

In this paper, we demonstrate that long-lived amplified spontaneous emission (ASE) action can be achieved in two transparent newly synthesized FPI waveguides (6F-6F and 6F-IMMDA, Scheme 1) doped with laser dye Pyrromethene 597 (PM597, Scheme 1) under 532 nm pumping. PM597 dye was chosen because it had been demonstrated to lase efficiently (PM597, Scheme 1) under 532 nm pumping. PM597 dye was converted into the fully imidized polyimide by treatment with a mixture of acetic anhydride/pyridine for 3 h at room temperature and 3 h at 60 °C. Both polyimides were isolated by precipitation on water, and purified by washing with ethanol several times. The polymers were then dissolved and precipitated once more to remove traces of solvent and oligomers, extracted in boiling ethanol for 12 h and dried overnight under vacuum at 120 °C. Yields were quantitative.

For thermal measurements, films were prepared from polyimide solutions in tetrahydrofuran (THF), with a 7.5% w/w polymer concentration. These solutions were cast on glass plates, and solvent was removed at 25 °C for 24 h. After peeling off the membranes from the glass, they were heated at 180 °C under vacuum for one day.

For optical measurements, asymmetric slab optical waveguides consisting of thin films of polyimides 6F-6F and 6F-IMMDA doped with laser dye PM597 and deposited onto the glass substrates, were prepared using the extender roller technique from chloroform solutions of both polyimides \((100 \text{ mg mL}^{-1})\) and the dye \((1\text{-}5 \times 10^{-2} \text{ M}).\) The substrate was 0.98 mm thick, the film thicknesses were 9 µm, and the dye concentration was \(2.5 \times 10^{-2} \text{ M.}\) For comparison, thin films of PMMA doped with PM597 with the same dye concentration and film thickness were also prepared.

**Experimental Part**

**Polymer Synthesis and Film Preparation**

Polyimides 6F-6F and 6F-IMMDA were prepared from hexafluoroisopropylidene diphthalic anhydride (6FDA) and the corresponding dianime, i.e., hexafluoroisopropylidenedianiline (6F) and 4,4’-methylenebis(2-isopropyl-6-methyl aniline) (IMMDA), respectively. Equimolar amounts of dihydride and dianime were first made to react at low temperature \((0 \text{ °C}/1 \text{ h} \text{ and for } 5 \text{ h at room temperature})\) to attain a solution of polyamic acid, which was then converted into the fully imidized polyimide by treatment with a mixture of acetic anhydride/pyridine for 3 h at room temperature and 3 h at 60 °C. Both polyimides were isolated by precipitation on water, and purified by washing with ethanol several times. The polymers were then dissolved and precipitated once more to remove traces of solvent and oligomers, extracted in boiling ethanol for 12 h and dried overnight under vacuum at 120 °C. Yields were quantitative.

Scheme 1. Repetition unit of the synthesized polyimides and PM597 dye structure.
Methods

Thermal properties were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC experiments were carried out in N₂ at 20° min⁻¹ on a Perkin-Elmer DSC-7 analyzer. Two scans were recorded on each sample, the first one from 50 to 200 °C, to eliminate any residual solvent or water absorbed, and the second one from 50 to 400 °C, to determine the range of glass transition temperature (T_g). TGA curves were recorded at 10° min⁻¹ in N₂ from 50 to 800 °C with a Perkin-Elmer TGA-7 analyzer on 2–3 mg samples. Inherent viscosities were measured on filtered 0.5 g·dl⁻¹ polymer solutions in N-methyl-2-pyrrolidinone (NMP) at 25.0 ± 0.1 °C, in an automated Ubbelohde viscometer.

The refractive indices of polyimides 6F-6F and 6F-IMMDA were measured using the Variable Angle Spectroscopic Ellipsometry (VASE) technique (ellipsometer M-2000DI from A. Woollam Co., Inc.), and found to be 1.5606 and 1.5723, respectively, at the dye emission wavelength. The refractive indices of PMMA and the glass substrate were measured at room temperature using an Abbe refractometer (Atago) employing 1-bromonaphthalene as sample-support interphase and a sodium lamp as monochromatic light at 589 nm, and found to be 1.4900 and 1.5176, respectively, at the dye emission wavelength.

Amplified Spontaneous Emission Measurements

The thin film samples were optically pumped at 532 nm with 20 ns full width at half maximum (FWHM) pulses from a frequency-doubled Q-switched Nd:YAG laser (Lotis TII SL-2132). The laser was operated at 1.5 Hz repetition rate except in the stability studies, where the repetition rate was 5 Hz. The pump radiation was horizontally polarized, which allowed controlling the pulse energy incident onto the sample by insertion into the pump beam path of a half-wave plate (HWP) and a linear polarizer (LP) set with its polarization axis horizontal. By rotating the HWP the linear polarization of the input beam is rotated out of the horizontal, and the pump beam is blocked more or less by the LP, depending on the rotation angle introduced by the HWP. Pump energy was measured with a calibrated Laser Energy Meter (QE 12LP-S-MB-DO, Gentec).

The light incident on the sample was perpendicular to the film surface and focused onto that surface in stripe shape of ≈150 μm width by a combination of negative and positive cylindrical quartz lenses (f = −15 and +15 cm, respectively), perpendicularly arranged. An adjustable slit was used to select only the central portion of the pump beam. An micrometer screw was allowed to precisely select the width of the slit. Excitation stripes of up to 2 mm length were defined, with an end placed right up to the edge of the film. The edge emission from the sample was collected with a 5 cm focal length spherical lens, focused onto a fiber bundle and detected with a spectograph/monochromator (SpectraPro-300i Acton Research) equipped with a thermoelectrically cooled CCD detector (SpectruMM:GS 128B). The sample was placed on a XY Motorized Translation Stage, computer controlled, to allow precise positioning.

Results and Discussions

As mentioned in the Experimental Part, FPI were prepared from a fluorinated dianhydride (6FDA) and two diamines by a two-step general procedure, which involves the formation of an intermediate polyamic-acid in a first step and the attainment of the final polyimide in a second step, through a chemical cyclodehydration reaction promoted by a mixture pyridine-acetonic anhydride. In this way, polyimides 6F-6F and 6F-IMMDA were obtained with high yield and high molecular weight, as it could be stated by measuring their inherent viscosity, η_inh (Table 1). Diamine IMMDA was chosen for this work as it is a non-planar monomer which bears side methyl and isopropyl groups, which in principle should provide a comparatively high free volume and, consequently, good solubility. The difference observed in the value of η_inh is consistent with the reactivity of the diamines against dianhydrides, and it confirmed that diamine 6F is much less nucleophilic than diamine IMMDA.

Relevant properties of the prepared polyimides are collected in Table 1.

Both polymers were soluble in suitable organic media, such as THF and chloroform, which helped in the preparation of dense films by traditional casting methods. The thermal properties of the polyimides, as evaluated by DSC and TGA, were actually very good, with T_g around 300 °C, much higher than traditional polymers such as acrylics or polycarbonates. Their resistance to high temperature was also outstanding, with initial decomposition temperatures around 500 °C, measured by dynamic TGA.

Thin films of polyimides 6F-6F and 6F-IMMDA doped with laser dye PM597 were deposited onto glass substrates,
defining an asymmetric structure consisting of the polymeric slab with refractive index \( n_1 \) surrounded by media of different refractive indices: air as the upper media with refractive index 1, and glass as the lower media with refractive index \( n_2 = 1.5176 \) at the dye emission wavelength. The refractive indices of polyimides 6F-6F and 6F-IMMDA at the dye emission wavelength are \( n_1 = 1.5606 \) and 1.5523, respectively, and total reflection takes place at the interface FPI/PM597-glass for light incident at angles greater than the critical angle \( \theta_c = \sin^{-1} \frac{n_2}{n_1} \approx 76^\circ \) and 78°, respectively. Thus, the air-FPI/PM597-glass structure defines an optical waveguide, where light incident at the film-glass interface at angles greater than \( \theta_c \) is totally reflected and guided along the length of the film. For comparison, thin films based on PMMA were also prepared. As the refractive index of PMMA \( (n_1 = 1.4900) \) is lower than that of glass, in this case no total reflection takes place at the film/substrate interface, and light leaks into the substrate. A leaky waveguide or quasi-waveguide is obtained, where light is confined by the film/air interface while the reflection at the film/substrate boundary is leaky. Although the optical properties of waveguides and leaky waveguides are not directly comparable, it is still possible to compare the photostability of the materials under laser irradiation.\(^{[43]}\)

Amplified spontaneous emission measurements were carried out as described in the Experimental section. When pumped at low intensities, the light emitted from the edge of the films exhibited a broad emission spectrum, with a FWHM in the range 35–40 nm and peak wavelengths of \( \approx 593 \) and \( \approx 590 \) nm for 6F-6F/PM597 and 6F-IMMDA/PM597, respectively. At pump intensities above a certain threshold value, the spectral width of the emitted light first decreases fast and then sets in at a value of about 10 nm (Figure 1). The intensity of the emission grows linearly with the pump intensity but with a distinct change in slope at pump threshold (Figure 2). As it is well known, the collapse of the FWHM in the emission spectrum and the change of the slope in the emission intensity with increase in the pump intensity are a signature of the onset of ASE emission above a certain pump threshold.\(^{[44,45]}\)

In Figure 2 we have used a log-log scale to better distinguish the different behaviors in the emission as a function of the pump intensity. From the data in Figure 2, it can be estimated a pump threshold for the onset of ASE emission of 90, 55, and 58 kW \( \cdot \text{cm}^{-2} \) for the waveguides based on polyimide 6F-6F, polyimide 6F-IMMDA, and PMMA, respectively. It can also be appreciated in Figure 2 a second change in slope in the emission from the films based on PMMA and polyimide 6F-IMMDA at pump intensities above 100 kW \( \cdot \text{cm}^{-2} \) indicating gain saturation. The pump intensity for the onset of saturation can be estimated to be 122 kW \( \cdot \text{cm}^{-2} \) for PMMA/PM597 and 147 kW \( \cdot \text{cm}^{-2} \) for 6F-IMMDA/PM597. For the waveguide 6F-6F/PM597, saturated behavior is not clear yet at pump fluences as high as 356 kW \( \cdot \text{cm}^{-2} \).

Amplified spontaneous emission gain measurements were carried out using the variable stripe length (VSL) method, which consists basically in pumping optically the sample with a stripe-shaped beam of variable length at constant intensity and measuring the intensity of the edge-emitted ASE as a function of stripe length.\(^{[46]}\) In the small-signal regime, the ASE intensity collected at the waveguide edge varies with the pump stripe length as:

\[
I(\lambda) = \eta g'(\lambda) \left( e^{g(\lambda)l} - 1 \right)
\]

where \( g'(\lambda) \) is the internal gain coefficient due to stimulated emission processes, \( g(\lambda) \) is the net gain coefficient, \( g(\lambda) = g'(\lambda) - \alpha \), with \( \alpha \) being the loss coefficient, \( l \) is the length of the pumped stripe, and \( \eta \) is a coefficient

![Figure 1. Dependence of the FWHM of the output emission spectra on pump intensity for a 2 mm length pumped stripe.](image1)

![Figure 2. Dependence of the intensity of the output emission on pump intensity for a 2 mm length pumped stripe. The dotted lines are a guide to the eye.](image2)
proportional to the spontaneous emission rate and to a geometrical factor that depends on the amplifier dimensions. Thus, \( g \) can be determined by plotting the intensity of the ASE emission as a function of the pumped stripe length and fitting the resulting curve to the expected dependence given by Equation (1).

Although Equation (1) is a common expression used in the literature to analyze the gain behavior of waveguides, its use should be restricted to pump energies low enough for saturation effects not being important. A usual approach consists in using Equation (1) to fit only those subsets of experimental data apparently free of saturation effects, but this procedure can lead to appreciable errors in the calculated gain coefficients. \[46\] If the ASE intensity reaches the saturation level, as is often the case, a better estimation of the gain coefficients is obtained by using the equation: \[46,47\]

\[
l = \frac{sl(\lambda)}{g(\lambda) + ng'(\lambda)s} + \frac{g(\lambda)}{[g(\lambda) + ng'(\lambda)s]^2} \times \ln\left[\frac{ng'(\lambda) + [ng'(\lambda)s + g(\lambda)]f(\lambda)}{ng'(\lambda)}\right]
\]  

(2)

where \( s \) is a gain saturation parameter (\( s = 1/I_s = \sigma_e \tau/\nu \), where \( \sigma_e \) is the emission cross section, \( \tau \) is the fluorescence lifetime, and \( \nu \) is the frequency of the ASE emission).

The polyimide-based samples were subjected to systematic measurements of the intensity of the emitted light as a function of excitation length for nine different pump intensities, from 11 to 530 kW \( \cdot \) cm\(^{-2}\). The data obtained are plotted in Figure 3, where each point in the graph is an average of four measurements. By fitting the experimental data to the expected dependence as given by Equation (2) (solid lines), the net gain coefficients at increase in the pump intensities are obtained. In Figure 4 are plotted the results obtained for the net gain coefficients as a function of the pump intensities. It can be appreciated that at pump intensities below \( \approx \)300 kW \( \cdot \) cm\(^{-2}\) the gain of the quasi-waveguide 6F-IMMDA/PM597 is higher than that of the waveguide 6F-6F/PM597. The situation reverses at higher pump intensities, where net gains of up to \( 93 \pm 4 \) cm\(^{-1}\) are obtained for the 6F-6F/PM597 waveguide, whereas in the 6F-IMMDA/PM597 quasi-waveguide the net gain coefficient levels off at about \( 68 \pm 3 \) cm\(^{-1}\).

As indicated above, plots such as those in Figure 2 allow for an estimation of the pump threshold for the onset of ASE emission. Nevertheless, the data in Figure 2 corresponds to a stripe of a given length, and thus, strictly speaking the estimated threshold values are just valid for that specific stripe length. A more accurate estimation of threshold values, independent of the pumped stripe length, can be obtained from the plots in Figure 4. Defining the threshold intensity for ASE emission as the pump intensity for which \( g = 0 \), we obtain from the data in Figure 4 threshold intensities of 65 and 30 kW \( \cdot \) cm\(^{-2}\) for 6F-6F/PM597 and 6F-IMMDA/PM597, respectively.

From a practical point of view, an important parameter in the behavior of the waveguides is the stability of the ASE emission under long time operation. For successful
operation and good performance, high resistance to dye degradation under repeated pumping is required. Dye degradation rate was assessed by pumping the samples at a fixed position with an intensity of 220 kW/cm² and a repetition rate of 5 Hz. The actual evolution of the intensity of the ASE emission of both polyimide waveguides as a function of the number of pump pulses is presented in Figure 5. For reference, it is also included in Figure 5 the evolution of the ASE emission from a waveguide with the same thickness and dye concentration but based on PMMA.

An important fact evident in Figure 5 is that the dye photostability is substantially greater in the polyimide-based films than when the host material was PMMA: after 40,000 pump pulses in the same position of the sample the emission output decreased to 50 and 23% of the initial value in the 6F-6F/PM597 and 6F-IMMDA/PM597 films, respectively, whereas in the PMMA-based film the emission dropped to 10% of the initial value after just 10,000 pulses. The relative stability of the different films can be better appreciated by considering the number of pump pulses necessary for the ASE emission dropping by 50%. In this regard, it is obtained that the ASE output drops to 50% of its initial value after 40,000, 14,100, and 1,160 pulses for the waveguides based on 6F-6F, 6F-IMMDA, and PMMA, respectively. This means that the 6F-6F-based waveguide is three times more stable than the 6F-IMMDA-based guide and 34 times more stable than the PMMA-based guide.

The improvement in photostability of the two FPI films with respect to the PMMA waveguide can be attributed mostly to differences in thermal properties between both polymer families. The thermal stability of the FPIs at least doubles that of the PMMA; hence, the heat transferred from the dye molecule to the matrix is more rapidly dissipated in FPI films, avoiding early thermal degradation of the dye. We have already seen this effect in bulk solid-state dye lasers, where the laser action of pyromethene chromophores incorporated into methacrylic and acrylic polymers was greatly enhanced by the presence of fluorine atoms into the structure of the organic monomers. Important increases in photostability due to enhancement of the thermal dissipation in the matrix provided by the presence of silica have also been observed in bulk solid-state dye lasers, when dye PM597 was incorporated into silicon-modified and organic-inorganic hybrid matrices.

To explain the differences between the two FPIs, additional aspects such as polymer chain density and fluorine content must be considered. The polyimide 6F-6F is denser than 6F-IMMDA (Table 1); thus, the polymeric free volume is lower and the average distance between dye molecules and polymeric chains is shorter in 6F-6F than in 6F-IMMDA. A higher proximity to the polymeric chains facilitates nonradiative energy transfer from the dye molecules to the polymeric chains decreasing thermal and photochemical (dye molecule radicalization via triplet states) degradation. An improvement in dye photostability when the polymeric free volume is reduced has already been seen in previous studies on dyes incorporated into polymeric bulk materials. On the other hand, pyromethene dyes incorporate fluorine atoms into their structure. This increases the compatibility of the dye molecules with the fluorinated matrix and favors the interactions between dye molecules and polymer. Polyimide 6F-6F incorporates more fluorine atoms than polyimide 6F-IMMDA, which should favor the stability of PM597 in the 6F-6F. Taken together, these mechanisms could explain the better performance of PM597 when incorporated into polyimide 6F-6F.

In a previous paper, we had obtained gains of up to 57 cm⁻¹ for waveguides based on PM597 incorporated into PMMA. The thickness of the films was the same as in the present work but the dye concentration was doubled (5 × 10⁻² mol). That gain is considerably lower than those obtained in the present work with the FPI-based thin films.
Under 532 nm pumping, gains of up to 40 cm\(^{-1}\) have been reported by Lu et al.,\(^{[10]}\) with optical waveguides based on polystyrene films doped with dye DCJTB pumped with pulses of 0.13 mJ. Gain of 52.71 cm\(^{-1}\) was obtained by Zhang et al.,\(^{[21]}\) with waveguides based in a mixture of dyes DCJTB and C545T in polystyrene films, with a pump energy of 0.08 mJ\cdot pulse\(^{-1}\). Djiang et al.,\(^{[20]}\) obtained net gain coefficients of 37.2 cm\(^{-1}\) with near-infrared-emitting dye LDS821 incorporated into poly(4-vinyl)-phenol, with 314 kW\cdot cm\(^{-2}\) pumping. Recently, Yuyama et al.,\(^{[21]}\) obtained gains of 14 cm\(^{-1}\) from FPI waveguides obtained from fluorinated-poly(amic-acids) precursors and doped with IR dye LDS950 dye under pumping at 337 nm with a pulse energy of 0.08 mJ, DCJTB and C545T in polystyrene films, with a pump energy of 1.160 pulses.

The net gains reported in the present work, of 68 and 93 cm\(^{-1}\) for waveguides 6F-6F/PM597 and 6F-IMMDA/PM597, respectively, were obtained at pump intensity of about 500 kW\cdot cm\(^{-2}\), which corresponds to 34 \mu J\cdot pulse\(^{-1}\) or 15 mJ\cdot cm\(^{-2}\). Thus, the gains exhibited by our FPI-based waveguides compare well or are higher than those obtained in similar systems reported in the literature.

**Conclusion**

In this paper, we demonstrate that replacing PMMA with FPI as host material for lasing dyes in active asymmetric planar waveguides improves substantially the photostability of the dye under laser operation. Relevant parameters to optimize the lasing performance of the guides are the polymer chain density and fluorine content. The guide with the higher fluorine content (6F-6F), demonstrated to be the most stable because 40 000 pump pulses of \(\approx 220\) kW\cdot cm\(^{-2}\) delivered at a repetition rate of 5 Hz were necessary for the ASE output dropping to 50% of its initial value. When the material in the thin film was based on PMMA, the ASE emission dropped to 50% of its initial value after just 1 160 pulses.

The observed thresholds for the onset of ASE emission in the FPI waveguides are of the order or higher than those reported in PMMA-based waveguides, but the much higher photostability exhibited by the FPI guides makes them very attractive from the point of view of practical applications. In addition to the higher photostability, the FPI waveguides also exhibit higher gains than those based on non-fluorinated polymers, with net gain coefficients of up to 93 cm\(^{-1}\).

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