

Plastic Optical Fibers with Gain and Switching

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Abstract — Novel plastic optical fibers (POF) based on polymethylmethacrylate, PMMA, doped with luminescent conjugated polymers and oligomers were fabricated. Our innovative approach is based on the chemical binding between the PMMA matrix and the dopant material as an alternative to the blending approach (mixture) of PMMA and the active material. We aimed at controlling load and dispersion of the luminescent polymer in the PMMA matrix, which are crucial for the optimisation of these optical media, while reducing the possibility of dopant segregation during the fiber drawing. Stimulated emission and optical switching inside the fiber were observed in some of the new materials, indicating that they can represent possible routes to plastic optical media, namely POFs, exhibiting gain and ultrafast switching.

I. INTRODUCTION

Plastic Optical Fibers (POFs) are becoming increasingly important for applications in local area networks and automotive applications, due to their advantages comparing to glass (silica) optical fibers (GOFs), namely low production costs, ease of optical coupling and flexibility [1,2]. Polymethylmethacrylate, PMMA, is the most widely used material for POFs. However, as shown in Figure 1, the attenuation is more than one order of magnitude higher than that of the silica fibers.

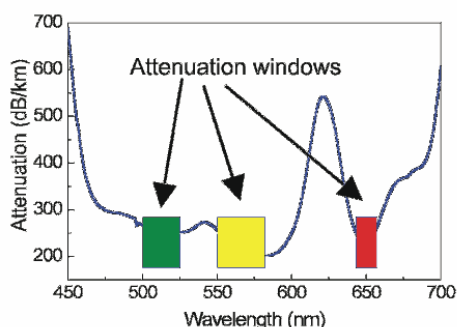


Fig. 1. Attenuation of PMMA and selected transmission windows

In GOFs the preferred transmission wavelengths (850, 1310 and 1550 nm) are chosen due to a combination of low loss wavelength windows and photodiodes sensitivity. The

most significant breakthrough in the GOFs applications for long distance data transmission was the discovery of amplification using Erbium (in the region of 1.5 μm).

Absorption is the major contribution for losses during light propagation across PMMA core, due to electronic transitions and, mainly, carbon-hydrogen vibrations. A significant improvement in POFs was the preparation of a polymer with fluorine instead of hydrogen atoms, named CYTOP (see Figure 2), developed at the Keio University by Prof. Y. Koike. POFs exhibiting, at some wavelength windows, even lower attenuation than GOFs were prepared and are in use. However, the price strongly limits its wide application.

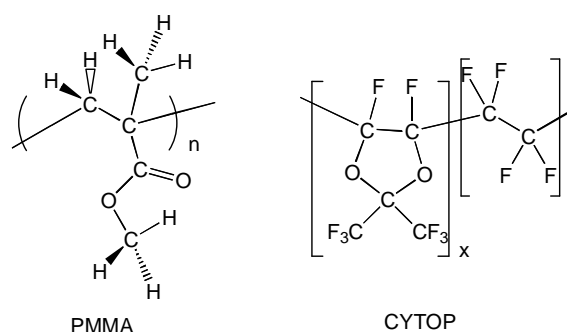


Fig. 2. Molecular structure of the repeat units of PMMA and of the perfluorinated polymer CYTOP®

Amplification could provide a means to circumvent the high attenuation of the much cheaper PMMA POFs.

Stimulated emission and lasing have been reported for various conjugated luminescent polymers. In view of the materials similarity in terms of properties and processing, these are ideal candidates to be dispersed within PMMA, using the stimulated emission to amplify the propagating signal.

A significant discovery towards this end was recently reported [3,4]. Studies of thin films made of a conjugated polymer known as PFO, dispersed in PMMA, showed that, indeed, stimulated emission occurs in the blue region (around 450 nm). The films were quite inhomogeneous. In the regions with low PFO content, it was also observed that, there was a shift of the gain region towards longer wavelengths (approaching the wavelength windows of PMMA low loss). Furthermore, impinging a second laser “push” pulse (780 nm, 150 fs), the stimulated emission was annihilated, recovering almost instantly ($\approx 1\text{-}2$ ps) at the end

of this “killing” pulse. This switching effect, could allow a signal modulation of about 300GHz.

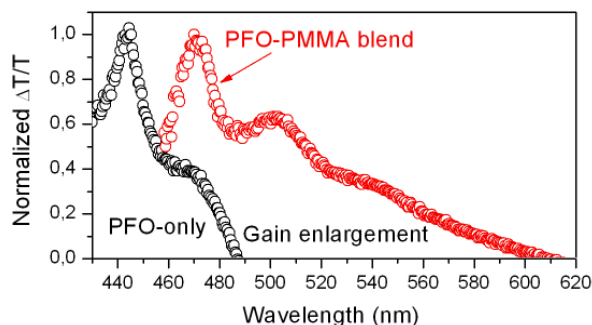


Fig. 3. Stimulated emission (gain) of pure PFO and of highly diluted PFO in PMMA (adapted from [5]), evidencing the gain enlargement upon dilution

The above observations with the PFO/PMMA system urged us to explore synthetic ways of introducing high contents of PFO and other conjugated polymers in the PMMA matrix, while keeping the conjugated polymers chains as isolated as possible, to transfer these properties into POFs.

Combination of all-optical signal amplification (as stimulated emission) and ultra-fast optical switching inside the fiber (gain killing using a short laser pulse and recovery within a few picoseconds) should yield high speed data transmission, much beyond the present maximum network speed for GOFs.

However, the tendency for phase separation in blends of PMMA and conjugated polymers is high. Our approach aims at circumventing phase separation by the use of a copolymer, as a single material, composed of blocks of PMMA and blocks of luminescent polymer, as a replacement for the use of blends.

II. RESULTS AND DISCUSSION

We have prepared several new luminescent polyfluorene derivatives which were functionalised in order to become reactive with the PMMA monomer (MMA). These reactive conjugated polymers were then inserted into the PMMA matrix upon copolymerisation with MMA (the monomer giving origin to PMMA) inside glass test tubes, which had to be broken at the end to recover the glassy material.

A. PFO-co-PMMA and derivatives

Figure 4 shows the route followed to prepare the final PFO-doped PMMA matrix. As final products we have obtained solid preforms (cylinders 2 x 20 cm) of the respective modified PMMA. The same reaction procedure was used to prepare a preform, from which POFs were drawn.

This first material was fully characterised in solution, as thin film and as the core of POFs. Importantly, the studies showed that the conjugated polymer was dispersed within PMMA, and it did not degrade during the fiber drawing (at about 200 °C).

Figure 5 shows the steady state emission (photoluminescence, PL) in the blue region of the spectrum, peaking at 440 nm. This spectrum is similar to those obtained for regular PFO (see Figure 6, solid line).

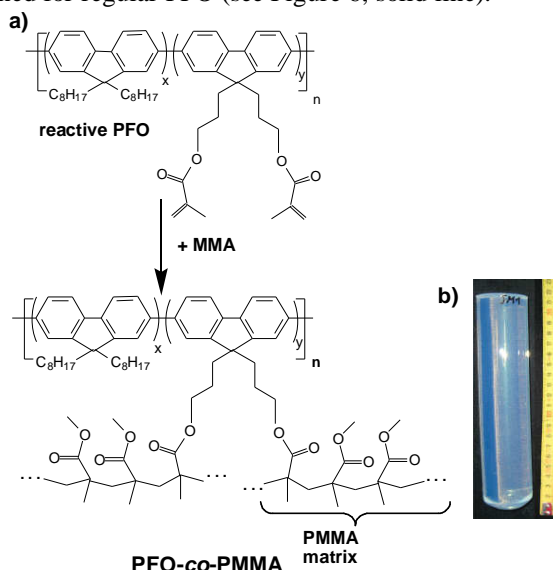


Fig. 4. a) Approach used to obtain PMMA doped with the luminescent polymer PFO, b) preform of the corresponding product (PFO-co-PMMA) prior to the fiber drawing

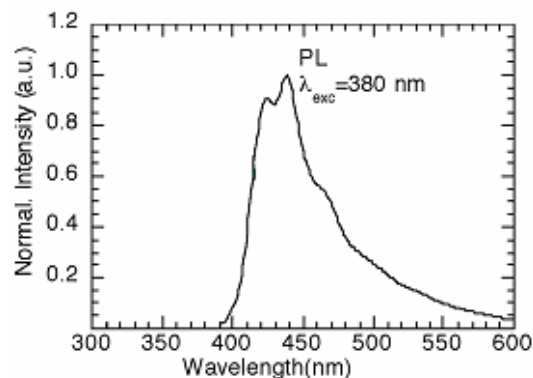


Fig. 5. Photoluminescence (PL) spectrum of a small piece of PFO-co-PMMA as obtained.

Figure 6 shows the differential transmission for films of the copolymer PFO-co-PMMA (squares) and for pure PFO film (dotted line). For comparison, the steady state PL spectrum for pure PFO is also shown (solid line). The details of these measurements can be found in Ref. 3-5. For pure PFO [6,7], there is stimulated emission (SE) (positive signal) from 450 to 500 nm and then photoinduced absorption, peaked at 580 nm assigned to absorption from separated charges generated upon excitation. For the new copolymer PFO-co-PMMA, there is SE extending up to 520 nm, evidencing gain enlargement in the PMMA matrix, as observed for the PFO-PMMA blends. However, due the low solubility of PFO in the copolymerisation media (MMA), the PMMA matrix is only slightly doped with PFO (~ 0.01 %) and the SE signal is weak. In spite of the very low concentration of the conjugated polymer, pump-push-probe

experiments, i. e. using a second excitation pulse at 780 nm, show evidence for optical switching (Figure 6 – insert). The SE recovery takes place within 2 ps after the push pulse.

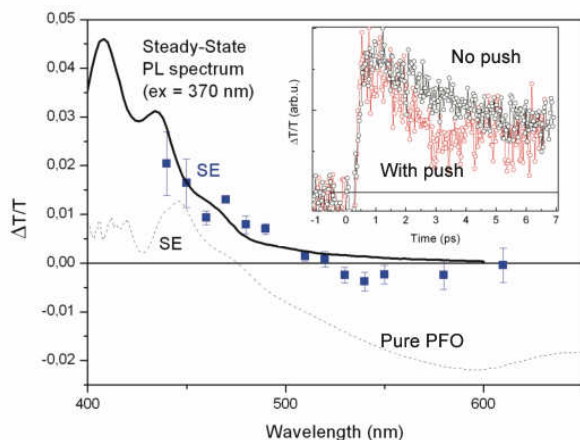


Fig. 6. Differential transmission ($\Delta T/T$) spectrum of the copolymer PFO-*co*-PMMA (squares) and for pure PFO. The steady state PL spectrum of pure PFO is also shown. The insert shows optical switching of the stimulated emission (SE) at 470 nm, which recovers within ca. 2 ps.

In spite of the low intensity of the SE signal generated in PFO-*co*-PMMA, these observations confirm the anticipated chain isolation. Similar results were also observed in POFs drawn from this copolymer.

Figure 7 shows the attenuation spectra of POFs with the core made of regular PMMA, PMMA blended with PFO (0.003%) and PFO-*co*-PMMA (with 0.003% by weight content of PFO). Surprisingly, the fiber based on PFO-*co*-PMMA is the one showing the highest attenuation. The explanation for this result is not yet clear.

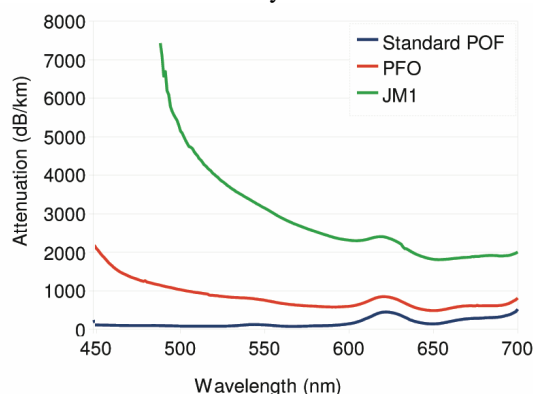


Fig. 7. Attenuation spectra of POFs based on pure PMMA (standard POF), on PMMA doped with regular PFO ("PFO") and on PFO-*co*-PMMA ("JM1").

In view of the low PFO content achieved with PFO-*co*-PMMA and as its gain region is to blue with respect to the low attenuation windows of PMMA [8], various derivatives have been prepared, aiming at increasing the solubility of the reactive conjugated polymer (to be copolymerised with MMA) and at shifting the stimulated emission towards

longer wavelength. POFs were produced with such various dopants, as shown in Fig. 8.

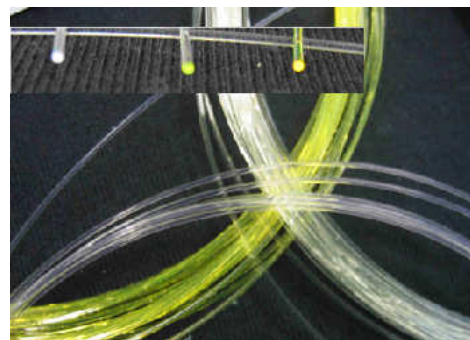


Fig. 8. Optical fibers made of PMMA doped with luminescent polymers. The different luminescence colours can be observed at the POF ends.

One of the prepared dopants with emission shifted to longer wavelengths (green) consisted on a copolymer combining bithiophene units, as low energy gap units, in the reactive chains of polyfluorene (referred to as PF2T). Also, we added lateral solubilizing groups to increase solubility in the copolymerisation media. Afterwards, we have carried out the copolymerisation reaction with MMA in similar conditions to those used for the preparation of the blue emitting PFO-*co*-PMMA. In fact, the new luminescent polymer showed increased solubility in the copolymerisation medium (ca. 0.27 %), which allowed us to obtain homogeneous samples with doped levels of 0.1 %, by weight. Figure 9 shows the steady state PL spectra of the reactive PF2T in solution and of the corresponding copolymer with PMMA.

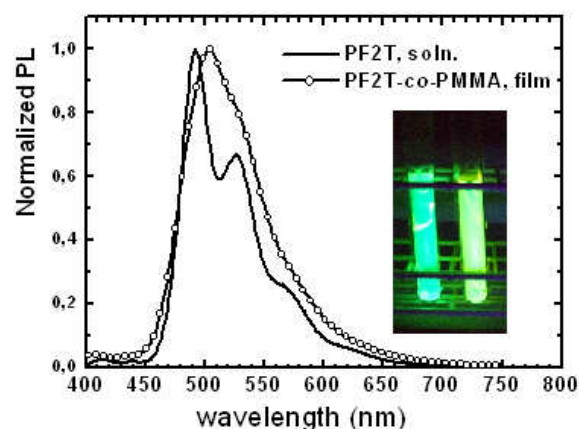


Fig. 9. Photoluminescence spectra of reactive PF2T in solution and of the corresponding PF2T-*co*-PMMA copolymer ($\lambda_{exc} = 380$ nm). The insert shows test tubes containing PF2T-*co*-PMMA under UV illumination.

The insert shows the glass test tubes (where the polymerisation reactions were carried out), containing 0.01 % and 0.1 % of the luminescent component, under ultraviolet (365 nm) illumination. The steady state PL emission for the new copolymer extends from 450 nm up to

650 nm, covering windows where attenuation of PMMA fibers is lower [8]. The characterisation of fibers prepared with these materials is in course.

B. 3SPF-co-PMMA

Aiming at improving the content of the active dopant in the PMMA matrix, we have prepared a copolymer based in PMMA and a new spirobifluorene compound, 3SPF-co-PMMA (Figure 10). Spirobifluorenes are highly fluorescent compounds, with typically high glass transition temperatures, which is favourable when aiming at preparing thermally stable films. Moreover, they typically show high chemical and thermal stability towards annealing and have demonstrated amplified spontaneous emission in the UV [9].

As a result, the synthesised reactive 3SPF showed a much higher solubility in the copolymerisation medium when comparing to the reactive PFO, allowing the preparation of homogenous samples with 0.1 %, by weight, of the luminescent material.

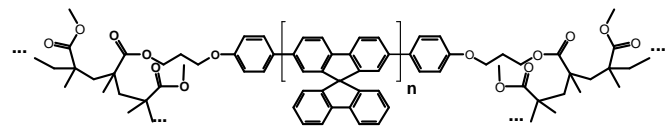


Fig. 10. Chemical structure of the copolymer 3SPF-co-PMMA

Figure 11 shows the steady state photoluminescence spectra of the reactive 3SPF compound in solution and of a solid film of the copolymer 3SPF-co-PMMA, containing 0.1 % of 3SPF. The similarity between the two bands indicates that the 3SPF chemical structure is not affected during the copolymerisation with MMA.

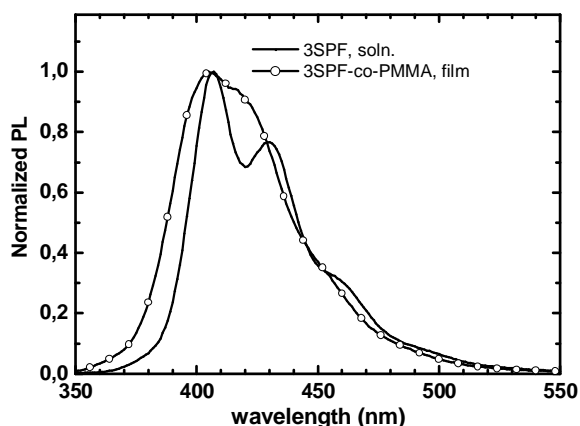


Fig. 11. Photoluminescence spectra ($\lambda_{exc}=333$ nm) of reactive 3SPF and 3SPF-co-PMMA (3SPF is ca. 0.1 %, by weight).

Stability studies showed that 3SPF-co-PMMA films are stable up to 150 °C for 3 hours, under room light and air. Studies on these material and POFs prepared with it are still in progress.

III. CONCLUSIONS

We have shown that the copolymerisation approach between a reactive luminescent material and MMA allows us to obtain homogeneously doped PMMA. Stimulated emission and optical switching were observed for PMMA doped with blue emitting PFO (PFO-co-PMMA). Upon adequate chemical modification of the conjugated polymer we could change the emission wavelength range and improve its solubility. PMMA doped with smaller molecules (oligomers), such as spirobifluorene compounds, are promising candidates for POFs exhibiting gain and ultrafast switching.

REFERENCES

- [1] J. Zubia and J. Arrue, "Plastic Optical Fibers: An Introduction to Their Technological Processes and Applications", *Optical Fiber Technology*, vol. 7, pp. 101-140, April 2001.
- [2] W. Daum, J. Krauser, P. E. Zamzow and O. Zeimann, *POF: Polymer Optical Fibers for Data Communication*, New York: Springer-Verlag 2002.
- [3] T. Virgili, D. Marinotto, G. Lanzani, and D.D.C. Bradley, "Ultrafast resonant optical switching in isolated polyfluorene chains", *Applied Physics Letters*, vol. 86, pp. 091113, February 2005.
- [4] T. Virgili, D. Marinotto, C. Manzoni, G. Cerullo, and G. Lanzani, "Ultrafast intrachain photoexcitation of polymeric semiconductors", *Physics Review Letters*, vol. 94, pp. 117402, 2005.
- [5] J. Morgado, A. L. Mendonça, A. Charas, J. Clark, G. Lanzani, L. Bazzana, A. Nocivelli, "Polyfluorene-PMMA copolymers for plastic optical fibers with gain", *Proc. of SPIE*, (2008), in press.
- [6] B. Kraabel, V. I. Klimov, R. Kohlman, S. Xu, H-L. Wang, and D. W. McBranch, "Unified picture of the photoexcitations in phenylene-based conjugated polymers: Universal spectral and dynamical features in subpicosecond transient", *Physics Review B*, vol. 61, pp. 8501-8515, March 2000.
- [7] T. Virgili, D. G. Lidzey, D. D. C. Bradley, G. Cerullo, S. Stagira, and S. De Silvestri, "An ultrafast spectroscopy study of stimulated emission in poly(9,9-dioctylfluorene) films and microcavities", *Applied Physics Letters*, vol. 74, pp. 2767, 1999.
- [8] T. Kaino, *Polymers for Lightwave and Integrated Optics*, Lawrence A. Hornak, Marcel Dekker, New York, 1992, Chap 1.
- [9] T. Spehr, A. Siebert, T. Fuhrmann-Lieker, J. Salbeck, T. Rabe, T. Riedl, H. H. Johannes, and W. Kowalsky, "Organic solid-state ultraviolet-laser based on spiro-terphenyl", *Applied Physics Letters*, vol. 87, pp. 161103, 2005.