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New Fluorinated Polymers Doped with BODIPY Chromophore as Highly Efficient and Photostable Optical Materials

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Fluorine is a remarkable element that can impart a wealth of interesting properties to a macromolecule which includes, but is not limited to, low surface energy, low refractive index, high thermal stability, and enhanced chemical resistance when compared to their nonfluorinated analogues.[1] Therefore, polymers that contain atomic fluorine in or along the backbone possess many desirable physical properties due to, mainly, their C−F energy bond (116 kcal/mol) higher than the C−H one (99 kcal/mol), low polarity, and relatively small size of the fluorine atom.[2]

A material's refractive index is of critical importance for applications such as optical waveguides and ophthalmic devices. With the need for mechanical strength, environmental stability, and a high optical damage threshold, fluoropolymeric-based materials offer excellent potential as alternatives to traditional optical materials. Other advantages over their inorganic counterparts include relative ease of processing, light weight, insensitivity to vibrational stress, and low cost. Nowadays, some commercial industries offer a range of low refractive index fluorinated monomers that can be associated with other conventional monomers tailoring the refractive index of the resulting copolymers.

Notwithstanding, some optical applications of the fluoropolymers, that is, host matrixes for solid-state dye lasers, could be limited by their high permeability to oxygen, low glass transition temperature, and fragility of the final material which renders difficult their mechanizing and polishing. A way to avoid these problems while maintaining the advantages of fluorinated matrixes could be the copolymerization of monomers containing fluorine atoms with pure organic monomers that offer some excellent properties as solid hosts for laser dyes (good solubility of organic dyes, high optical homogeneity, adaptability to techniques of cheap production, ease of control over the structure, and chemical composition).

With this aim, in this letter we report on the laser action of a BODIPY chromophore, marketed as pyrromethene 597 (PM597) dye (Figure 1) dissolved in copolymers of methyl methacrylate (MMA) with a high fluorine-containing monomer, the 2,2,3,3,4,4,4-heptafluorobutyl methacrylate (HFMA; Figure 1) added in low proportion which allows us to obtain fluorinated materials with the mechanical, optical, and solvation properties appropriate to sustain efficient and stable laser oscillation in the solid state.

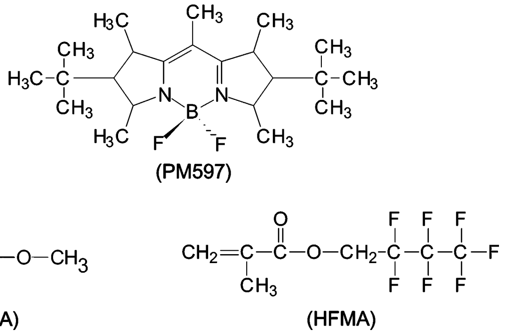

Figure 1. Molecular structure of PM597 dye, organic monomers MMA and HFMA.

PM597, in a concentration of 7×10^{-4} M, was dissolved in a fluorinated monomeric mixture of MMA/HFMA (70:30, v/v proportion of each monomer), which is the maximum content of HFMA incorporated in the copolymer that allowed the synthesis of monoliths under proper conditions, without suffering break and maintaining good optical and mechanical properties. The synthesis route followed to prepare the MMA/HFMA polymers was carried out by radical bulk polymerization using the thermal initiator 2,2′-azobisisobutyronitrile (AIBN) in an appropriate concentration (0.5 wt %) with regard to the total amount of monomers present in the initial mixture. AIBN is the thermal polymerization initiator of choice because it leaves UV-transparent end groups on the so-obtained copolymer. The monomer mixture with the dissolved dye was poured into polypropylene cylindrical molds, heated in an oven at 45 °C for 1−2 weeks, and then subjected to a slow increase of temperature, until reaching 80 °C, for 1 week. Finally, the temperature was reduced in steps of 5 °C per day until room temperature was reached, and only then were the samples unmolded. The solid monolith laser samples were cast in a cylindrical shape, forming rods of 10 mm diameter and 10 mm length. A cut was made parallel to the axis of the cylinder to obtain a lateral flat surface of $\approx 6 \times 10$ mm^2. This surface and the ends of the rods were polished until optical-grade finishing.

The copolymer distribution obtained was random and yields a molecular weight of about 2.1×10^6 g/mol, checked by GPC. As seen in Figure 1, there are seven atoms per HFMA monomer repetition unit, which appear as side substituents. This means that the concentration of fluorine atoms was 18.04 wt % in the P(MMA/HFMA, 7/3) formulation. Absorption and transmittance spectra of MMA and HFMA were identical over the visible range, and the absorption band of PM597 dissolved in this fluorinated polymer, centered at 524.1 nm, overlaps with that registered in liquid solution and does not exhibit any degradation signs. Refractive indices at 589 nm, measured using an ABBE refractometer (Carl-

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(1) Reisinger, J. J.; Hillmyer, M. A. *Prog. Polym. Sci*. **2002**, *27*, 971.

(2) Lezzi, R. A. In *Modern Fluoropolymers*; Scheirs, J., Ed.; John Wiley & Sons, Ltd.: Chichester, 1997; p 272.

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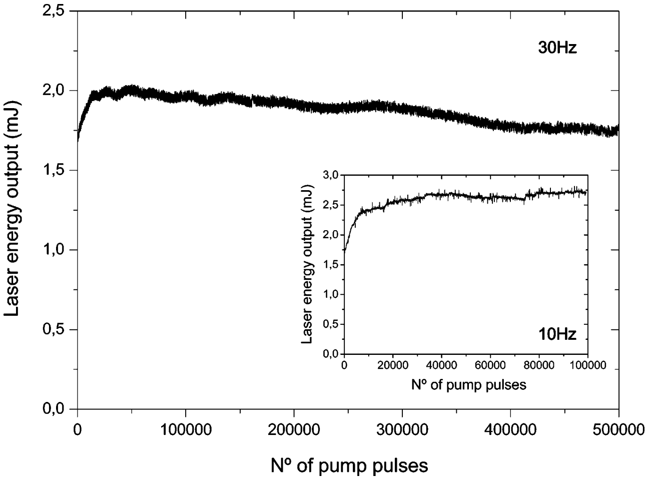

Figure 2. Laser energy output as a function of the number of pump pulses for PM597 incorporated in fluorinated copolymers of P(MMA/HFMA 7/3) under different experimental conditions: pump energies and repetition rates of 5.5 mJ/pulse and 10 Hz and 3.5 mJ/pulse and 30 Hz, respectively. Dye concentration: 7×10^{-4} M.

Zeiss), were 1.4850 (PMMA), 1.3670 (PHFMA),[3] and 1.4502 for the copolymer P(MMA/HFMA 7/3), respectively. The solid laser samples were transversely pumped at 532 nm with 5.5 mJ, 6 ns full width at half-maximum (fwhm) pulses from a frequency-doubled *Q*-switched Nd:YAG laser (Spectron SL284G) at a repetition rate of 10 Hz, and at 30 Hz with 3.5 mJ, 10 ns fwhm pulses from a diode-pumped, frequency-doubled, *Q*-switched Nd:YAG laser (Monocrom EO Q-DPSSL 532-12) under otherwise identical experimental conditions. Appropriate lenses focused the exciting pulses onto the lateral flat surface of the sample to form a line of about 0.3 × 10 mm. The oscillation cavity, with a length of about 2 cm, was formed by a flat aluminum mirror and the end face of the cylindrical sample as the output coupler. Details of the experimental system can be found elsewhere.[4]

Despite the low fluorescence quantum yield ($\Phi_f = 0.49$) of PM597 in a fluorinated solvent such as 2,2,2-trifluoroethanol,[5] a laser emission centered at 578 nm with an oscillation bandwidth (fwhm) of 6 nm and with a lasing efficiency of 35.6% was obtained from the dye doped P(MMA/HFMA 7/3). Although lasing efficiencies as high as 43 and 60% have been reported for PM597 incorporated into hybrid xerogel matrixes[6] and ormosil glass samples,[7] respectively, those efficiencies were obtained under longitudinal pumping in optimized laser cavities, whereas in the present work less efficient transversal pumping and an unoptimized resonator cavity were selected.

However, the most important feature of PM597 incorporated into this fluoropolymeric material is its high photostability, because no signs of degradation were observed in the laser output after 100 000 pump pulses at 10 Hz in the same sample position (Figure 2). The observed increase in the laser output during the first 10 000 pump pulses has been previously exhibited by other pyrromethene dyes incorporated into silica gel matrixes.[6] At the present time we cannot offer any nonspeculative explanation of this result, and further studies in progress would be necessary to clarify this point, although a priori no single cause is expected to fully explain the behavior of these rather complicated systems.

To assess the long-term stability of this matrix, it was subjected to a longer run of pumping under more drastic conditions. Thus, the sample was pumped at 30 Hz in the same position until a downward slope tendency in the laser stability was detected. In previous studies, we presented evidences showing that the accumulation of heat into the material in polymeric solid state dye lasers increased significantly with the pump repetition rate, impairing lasing stability.[8] However, some potential and new important applications of solid-state dye lasers, such as photodynamic therapy, would require the laser energy to be applied in high repetition rate pulses.

Under these more demanding conditions, the matrix exhibits again an excellent photostability because the laser output only decreases by 6% after 500 000 pump pulses (Figure 2). The best previous result was obtained for Nung et al,[6] with PM597 incorporated into hybrid xerogel matrixes, reporting a drop in the laser emission to 75% of its initial value after only 100 000 pump pulses but under softer experimental conditions (longitudinal pumping at 532 nm, with 1.8 mJ/pulse and a 10 Hz repetition rate) than those selected in the present work. Thus, the photostability exhibited in our system is, to the best of our knowledge, the highest achieved to date for solid-state dye lasers in organic, inorganic, or hybrid matrixes doped with any laser dye without rotating or translating the medium to distribute the thermal load over a large volume.

The results presented in this work indicate that the laser operation of solid matrixes doped with BODIPY chromophores is greatly enhanced by properly incorporating fluorine atoms into the structure of the material. While improving the thermal properties of the material its organic character remains, which means plasticity and easier synthesis than that shown by hybrid materials. The design and synthesis of new fluorinated polymers opens new challenges for the science of materials and enhances novel properties, economic processes, and innovative applications, especially in optoelectronic and biophotonic fields.

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(3) Seferis, J. C. *Polymer Handbook*, 4th ed.; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; John Wiley & Sons, Inc.: New York, 1999; p VI/571.

(4) Costela, A.; García-Moreno, I.; Sastre, R. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4745.

(5) Bañuelos Prieto, J.; López Arbeloa, F.; Martínez Martínez, V.; López Arbeloa, T.; López Arbeloa, I. *J. Phys. Chem. A* **2004**, *108* (26), 5503.

(6) Nung, T. H.; Canva, M.; Dao, T. T. A.; Chaput, F.; Brun, A.; Hung, N. D.; Boilot, J. P. *Appl. Opt.* **2003**, *42*, 2213.

(7) Reisfeld, R.; Weiss, A.; Saraidarov, T.; Yariv, E.; Ishchenko, A. A. *Polym. Adv. Technol.* **2004**, *15*, 291.

(8) Duchowicz, R.; Scaffardi, L. B.; Costela, A.; García-Moreno, I.; Sastre, R.; Acuña, A. U. *Appl. Opt.* **2003**, *42*, 1029.