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PHOTONIC CRYSTALS DOPED WITH PERYLENEDIIMIDE FOR LASER APPLICATIONS

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The aims of this study consist in the fabrication of polymeric photonic crystals (PCs) doped with perylenediimide (PDI) derivatives. Monodisperse core-shell polymer particles doped with PDI have been obtained by a terpolymerization process using a soap-free emulsion. The components of the emulsion were styrene, acrylic acid and a PDI chromophore presenting a methacrylate functional group. The polymer colloids allowed the fabrication of PC structures that have been investigated by SEM, UV-Vis and fluorescence spectroscopy. The PDI chromophore participation in the polymerization process modifies the latex properties such as polymer colloids size and, therefore, the optical properties of the photonic crystals. A lasing effect has been put into evidence using a "sandwich" type structure comprised of photonic crystals.

Keywords: photonic crystals, perylenediimide, soap-free emulsion polymerization, fluorescence, laser effect

1. Introduction

Photonic crystals (PCs) constitute a fascinating class of materials that can present many practical applications involving light interaction and manipulation [1-4]. They are generally characterized by nanostructures with a periodic dielectric arrangement that obstructs propagation of light in one or more directions for a given frequency range, called photonic stop-bands or band gaps (PBG) due to Bragg diffraction [5, 6].

Perylene-3,4:9,10-bis(dicarboximide) (PDI) derivatives are chromophores used as dyes and pigments in a wide variety of applications thanks to their exceptional high chemical, thermal and photochemical stability [7]. Also, due to their outstanding photophysical and photochemical properties characterized by high quantum yield of photoluminescence close to unity, PDI derivatives

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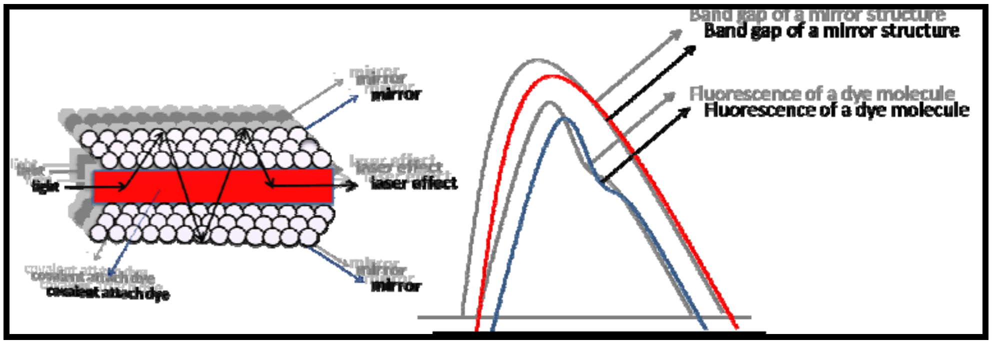
represent one of the most widely studied classes of organic semiconductors with potential applications as fluorescent dyes [8], near-IR dyes [9], optical and molecular switches [10, 11], artificial photosynthetic systems [12] as well as molecular wires [13], photosensitizers [14, 15] and as laser dyes [16].

Dye doping methods of PCs can consist of impregnation with chromophore solutions [17], swelling and deswelling process of the polymer colloids [18], emulsion polymerization using water-soluble dyes [19], encapsulation of hydrophobic molecules [20] and grafting on the surface [21]. Another approach consists in the synthesis dyes with polymerizable functional groups.

A lasing effect can be obtained by using the following elements: a material that provides optical gain through stimulated emission and an optical cavity that partially traps the light. Polymeric PCs can strongly modulate light, exhibiting photonic band gaps (PBG) or stop band domains (forbidden wavelength domains for light propagation) that arise due to the dielectric contrast of the constituents (colloids and air). The position of the PBG can be tuned by control over the size of the particles and periodicity of the assemblies. The doping of PCs with fluorescent dyes allows the investigation of the stop-band influence on the photoluminescence properties. Near the stop-band of PCs, the light propagates at reduced group velocities due to resonant Bragg scattering, which can enhance luminescence owing to stimulated emission and amplify the incident light absorption. The control of PCs structural parameters can allow access to a modulated laser emission using chromophore doped materials [3, 22-25]. By selecting the doping method and adjusting the colloidal PCs structure, the optical properties of the chromophore can be enhanced, modified and used for tuning the surface laser emission.

The novelty of this study consists in the synthesis of a new methacrylate derivative of perylenediimide and its utilization for the manufacturing of polymer PCs. Through a soap-free emulsion terpolymerization process of styrene, acrylic acid and the PDI methacrylate derivative, polymer colloids presenting covalently attached dye molecules in the polymer matrix were obtained.

The aim of this study was the realization of a lasing effect through the amplification of dye fluorescence as result of multiple reflections, caused by the superposition of the photonic structure band-gap and chromophores emission wavelength. The device utilized for this purpose has a “sandwich” type structure with the polymer particles doped with covalently attached dye molecule at the middle and with PCs on each side. A condition for fluorescence enhancement is that the excitation wavelength should be in the range of the stop-band of the PCs (Scheme 1 – Fabry-Perot type design of our device [26]).



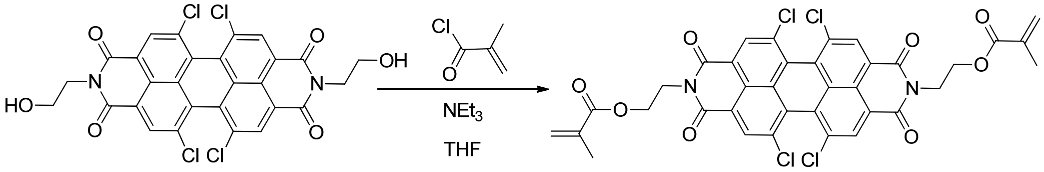
Scheme 1: "Sandwich" type device structure used for the lasing effect experiments

The advantages of a lasing effect obtained through the above described method are: the chemical bonding of the dye (its participation in the terpolymerization reaction) and a low price and simplicity of the device used to put into evidence the lasing effect.

2. Experimental

2.1. Materials

Latexes containing polymer colloids have been synthesized according to a single-stage polymerization process based on the formation and growth of polymeric nuclei dispersed in an emulsion consisting of water, styrene (ST), acrylic acid (AA) and potassium persulfate (KPS). Styrene (Merck) and acrylic acid (Merck) have been purified through vacuum distillation. Potassium persulfate (Merck) has been recrystallized from an ethanol/water mixture and then vacuum dried. The methacryloyl chloride, tetrahydrofuran and triethylamine were used as received. The N,N′-Bis(2′-hydroxyethyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-bis(dicarboximide) was obtained according to previous methods [27] and in a subsequent reaction with methacryloyl chloride was transformed into the methacrylate monomer utilized for soap-free emulsion terpolymerization process. The synthesis of the PDI monomer unit is presented in Scheme 2.

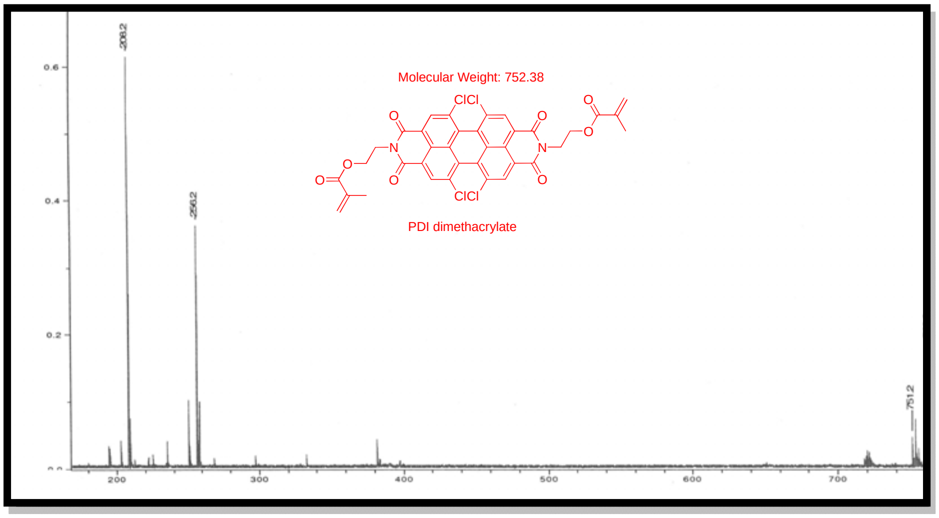


Scheme 2: The structure of the chromophore N,N′-Bis(2′-hydroxyethyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-bis(dicarboximide) and the synthesis of the methacrylate derivative

2.2. Methods

2.2.1 The synthesis of the PDI monomer

0.5 g N,N′ - Bis(2′-hydroxyethyl) - 1,6,7,12 – tetrachloroperylene - 3,4 : 9,10 - bis(dicarboximide) [27] was dissolved in 40 mL tetrahydrofuran. In the chromophore solution, 0.2 mL methacryloyl chloride was added in the presence of 0.1 mL triethylamine. The reaction mixture was kept to 40°C for 4 hours and after cooling most of the solvent was removed under reduced pressure. The reaction mixture was then washed with water and extracted with dichloromethane. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The product was separated by column chromatography on silica gel using CH_2Cl_2 and CH_2Cl_2/MeOH 10/0.1 as elution systems (0.3 g red powder, 55% yield). Maldi-ToF analysis is presented below (Scheme 3). The specific peaks put into evidence the synthesis of a compound with molecular weight of 752.38 g/mol.



Scheme 3: MALDI-ToF analysis of the PDI dimethacrylate derivative

2.2.2 Preparation of the ST-AA Colloidal Dispersion (A)

6.5 mL of ST and 2 mL of AA were added to 100 mL of distilled water containing 62.5 mg of KPS. The reaction mixture was purged with nitrogen and then maintained for 8 h at 75°C under continuous stirring. The final dispersion was dialyzed in distilled water for 7 days, using cellulose dialysis membranes (molecular weight cut-off: 12 000-14 000 Dalton), in order to remove the unreacted monomers and initiator.

2.2.3. Preparation of the ST-AA-PDI Colloidal Dispersion

A mixture of 6.5 mL of ST and 25 mg of PDI (PDI 1) (B), 35 mg (PDI 2) (C), 50 mg (PDI 3) (D), 70 mg (PDI 4) (E), respectively, was added to 100 mL of distilled water containing 62.5 mg of KPS and 2 mL of AA. The reaction mixture was purged with nitrogen and then maintained for 8 h at 75^{o}C under continuous stirring. The final dispersion was dialyzed in distilled water for 7 days, using cellulose dialysis membranes (molecular weight cut-off: 12 000-14 000 Dalton), in order to remove the unreacted monomers and initiator.

2.2.4. Preparation of the PDI Film

A 10^{-2} mol·L^{-1} solution of PDI in carbon tetrachloride was prepared, and the PDI was deposited on a glass substrate by a dip-coating method.

2.3. Characterization

The morphologies of polymer particles have been investigated through XL-30-ESEM TMP scanning electron microscope (SEM). Microphotographs were obtained using an optical microscope (Olympus, BX-41) equipped with a CCD camera. The UV-VIS spectra were recorded using a V-500 Able Jasco spectrophotometer. The fluorescence spectra were registered using a FP-6500 Able Jasco spectrofluorimeter. Matrix-assisted laser desorption-ionization (time-of-flight) mass spectrometry (MALDI-TOF) was performed on a Bruker Biflex III MALDI-TOF spectrometer operating in the positive reflection mode and dithranol used as the matrix. The emission properties of the device were evaluated using second-harmonic light at 532 nm from a Q-switched Nd:YAG laser beam (New Wave Research, Polaris II 20ST, Fremont, CA). The pulse duration was 3 ns and the repetition frequency was 10 Hz. The excitation pulse energy was controlled by using a combination of a k/2 plate, a polarizing prism, and neutral-density filters, and it was monitored by using an energy analyzer equipped with a pyroelectric sensor.

3. Results and discussions

The first stage in our study consisted in preliminary characterization of the obtained films using optical microscopy (Fig. 1). In all cases the presence of coloration is due to the diffraction properties [28] of the layers, which can suggest the existence of a periodic arrangement. Also, the red color is specific to the PDI dye. The distance between the defaults does not exceed 50 μm, specific to fine organized PCs structures [29].

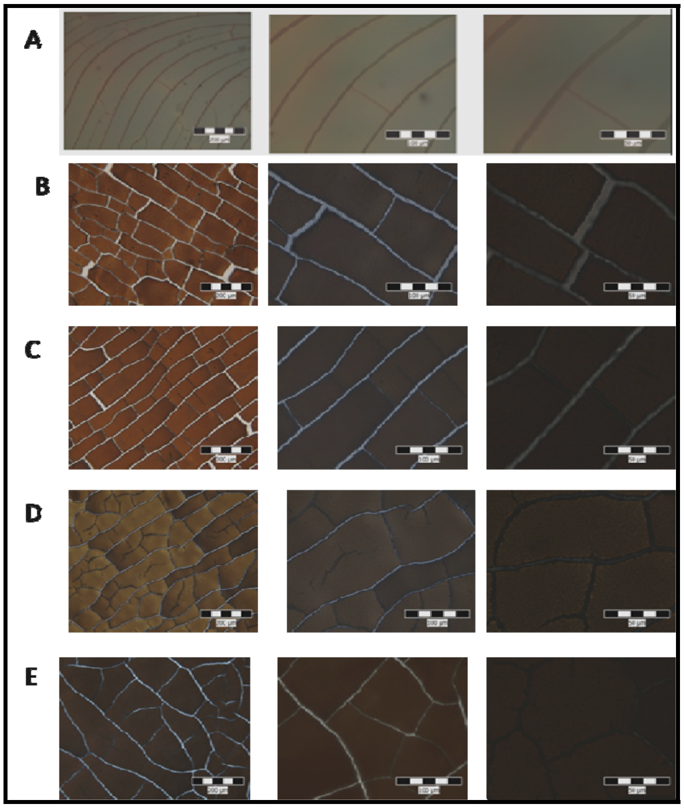
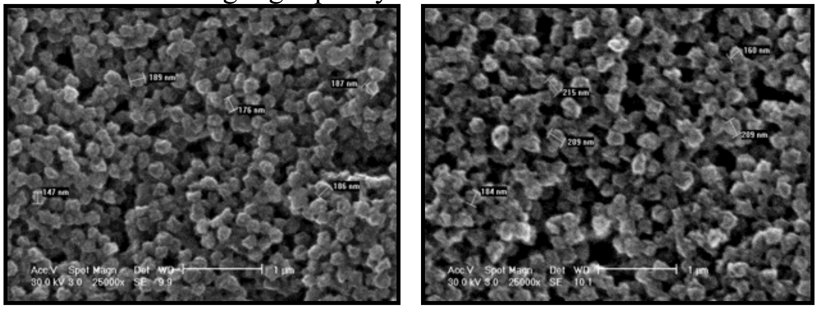
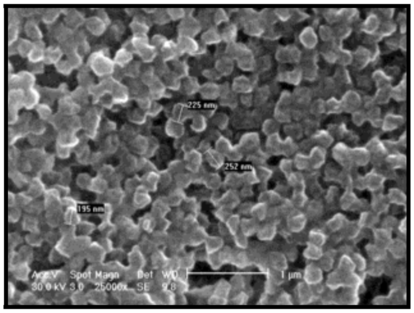


Fig. 1: Microphotographs of the obtained PCs films A) ST-AA; B) ST-AA-PDI 1; C) ST-AA-PDI 2; D) ST-AA-PDI 3; E) ST-AA-PDI 4

The colloidal PCs are characterized by dimensional monodispesity. In order to assess this characteristic, the obtained latexes have been characterized by SEM (Fig. 2). Thus, for the system **(B)** the particles size was determined as 186 nm, for **(C)** 209 nm and for **(D)** 225 nm. The most important parameter to note is the dimensional monodispersity obtained in all the cases, which is considered a good premise for obtaining high quality PCs.



a) b)



c)

Fig. 2: SEM analysis for: a) ST-AA-PDI 1; b) ST-AA-PDI 2; c) ST-AA-PDI 3;

In order to determine the band-gap characteristics of the obtained materials UV-VIS spectroscopy was used. The Fig. 3 reveals the existence of a stop-band in all five cases. Thus, a reflection band was registered at around 540 nm for the system (**A**), 560 nm for the system **(B)**, 575 nm for the system **(C)**, 580 nm for the system **(D)** and 590 nm for the system **(E)**. The presence of PDI is put into evidence by the absorption band at 530 nm in the cases **B-E**.

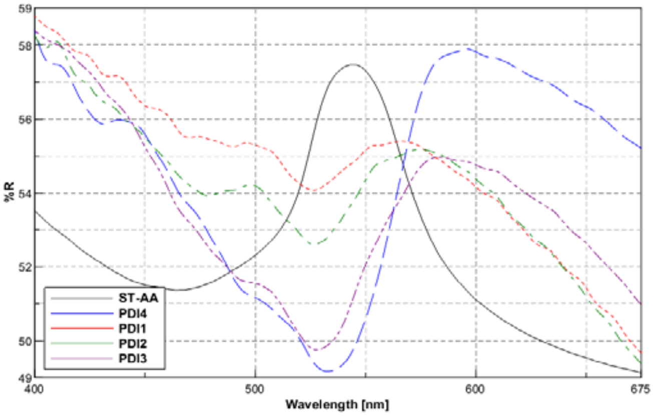
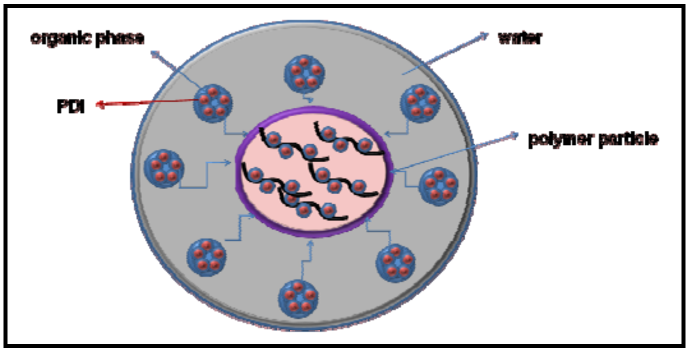


Fig. 3: UV-VIS spectra for: a) ST-AA; b) ST-AA-PDI 1; c) ST-AA-PDI 2; d) ST-AA-PDI 3; e) ST-AA-PDI 4

The band gap modifications are in accordance with the SEM measurements for the polymer particle sizes.

Considering previous studies [20, 30], the existence of nanoparticles or small molecules in organic phase, leads to a polymer particles size decrease due to inhibition effect. In this case, during the doping process the PDI actively takes part in the polymerization reaction through the methacrylate functional groups. Thus, a soap-free terpolymerization process was more efficiently realized compared to the copolymerization of ST-AA. Previous results where PDI dye was only solubilized in the organic phase revealed a particle size decrease [20, 31], whereas in this case a contrary effect is noticed. This can be explained by several factors such as: a) penultimate effect in terpolymerization (steric effect induced by the presence of PDI) and b) macroradicals water solubility reduction due to the presence of PDI into their structure. Thus, a higher number of low molecular weight macroradicals is generated. Colloidal stability is achieved through micellar nucleation. The number of nuclei is influenced by the macroradicals solubility, thus improving the concentration of PDI used in the process. Larger amounts of PDI involve the generation of macroradicals with lower molecular weight that achieve colloidal stability by the aggregation of a high number of macroradicals, resulting in a lower number of nuclei, and therefore an increased particle size (see Scheme 4).



Scheme 4: Polymer particles formation in aqueous phase

Another important characteristic of the obtained materials is represented by their fluorescence properties. It was previously reported that the PCs may act as a Bragg mirror and can effectively increase fluorescence intensity of organic dyes because they enhance excitation and/or emission [32]. The study of the emission characteristic gives an insight on the PDI organization inside the polymer matrix. The investigations of the presented PC films doped with PDI revealed a fluorescence emission close to the monomeric state of the dye [31] (Fig. 4). Thus, the obtained materials are excellent candidates for lasing effect studies, the lack of aggregates leading to more efficient emission amplification. In contrast, aggregates formation is noticed and the signal shifts to a value around 560 nm for the PDI solid film. A condition for fluorescence enhancement is that the excitation wavelength should be in the range of the stop-band of the PCs. The excitation light reflected by a Bragg mirror can stimulate more dye molecules, which is also in favor of fluorescence enhancement. In our case, the emission wavelength (550 nm) is lower than the maximum reflection value of the stop-band (560 - 590 nm) (Fig. 3).

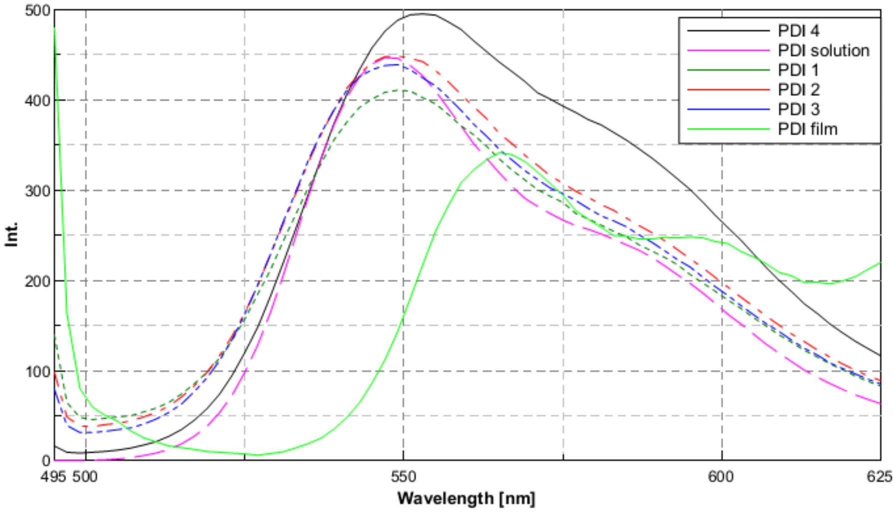


Fig. 4: Fluorescence spectra for ST-AA-PDI 1; ST-AA-PDI2; ST-AA-PDI3; ST-AA-PDI4, PDI in solution CH_2Cl_2 10^{-6}M and PDI solid film

Other series of experiments consisted in the construction of the sandwich type structure and lasing effect determinations. ST-AA polymer colloids have been utilized as mirror layers while as active layer ST-AA-PDI 1 was used. The results are presented in Fig. 5.

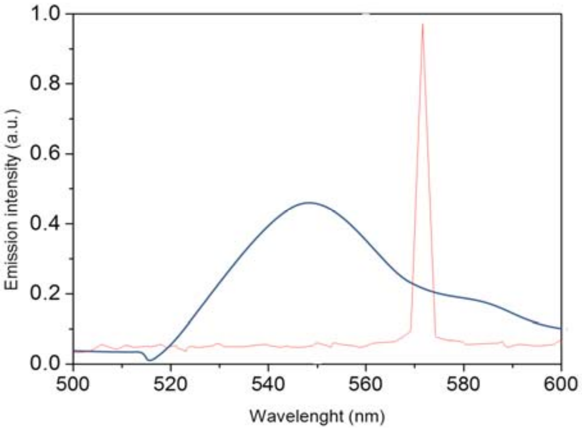


Fig. 5: Fluorescence spectra of the PDI doped PCs (using an excitation wavelength of 485 nm) and emission amplification using a 532 nm laser diode

When the excitation energy was increased to 210 nJ $pulse^{-1}$, a laser-emission peak could suddenly be observed at 570 nm. The intensity value of the laser emission is almost double than the emission of ST-AA-PDI 1. The width of registered signal sustains the lasing type emission.

4. Conclusions

Monodisperse core-shell polymer particles doped with PDI have been obtained by employing a soap-free emulsion terpolymerization process of styrene, acrylic acid and a PDI chromophore (this presenting a methacrylate functional group). The size of the particles is influenced by PDI concentration. The investigations of the presented PC films doped with PDI revealed a fluorescence emission close to the monomeric state of the dye. A device comprised of a "sandwich" type structure presenting at the middle the sensitive material (the polymer particles with covalently bonded dye molecules) and at each side, photonic crystal structures with band-gaps with emission wavelength domain of the chromophore was manufactured. Upon excitation of this device narrow emission amplification was registered confirming the lasing effect generation.

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