



Monomer type emission of perylenediimide derivatives doped polymer particles

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ABSTRACT

This study aims to present the fabrication of colloidal photonic crystals (PCs) doped with perylenediimide (PDI) derivatives. Monodisperse PDI doped core-shell polymer particles have been obtained by employing a soap-free emulsion polymerization process of styrene and 2-hydroxyethylmethacrylate with the chromophore solubilized in the organic phase. The obtained polymer colloids allowed the fabrication of PC films that have been investigated by UV-vis and fluorescence spectroscopy. The hybrid materials have been investigated in comparison with PCs doped by the classical impregnation method. Thus, the doping using soap-free emulsion polymerization resulted in the obtaining of PDI doped core-shell polymer particles exhibiting monomer emission, whereas by employing an impregnation doping method H-type aggregates are formed.

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1. Introduction

Polymer chemistry permits the obtaining of monodisperse nanoparticles capable of crystal lattice formation, thus allowing the manufacturing of colloidal photonic crystals (PCs). PCs present a periodic dielectric arrangement which does not allow propagation of light in all directions for a given frequency range, due to Bragg diffraction, resulting in stop-bands or band gaps formation [1–3].

Soap-free emulsion polymerization [4–9] represents one of the most promising methods in polymer chemistry that allows the synthesis of sub-micronic polymer colloids. Colloidal particle films can be obtained by various methods, such as gravitational sedimentation [6], centrifugation, vertical deposition [10], spin-coating [11], physical confinement, interfacial [12] or electric field induced self-assembly [13].

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 [14]. Also, due to their outstanding photophysical and photochemical properties characterized by high quantum yield of photoluminescence close to unity, PDI derivatives represent one of the most widely studied classes of organic semiconductors with potential applications as fluorescent dyes [15], near-IR dyes [16], optical and molecular switches

[17,18], artificial photosynthetic systems [19] or molecular wires [20], photosensitizers [21,22] and lasers dye [23].

The properties of the versatile PDI chromophore can be easily fine tuned by introducing suitable substituents in the 1, 6, 7 and 12 positions, the so-called bay positions [24] to exhibit quite diverse electronic and optical properties [25]. Nevertheless, crystallographic structures of PDI derivatives substituted at the bay region are characterized by a twist of the carbon framework resulting from repulsion and steric effects among the substituents [26,27].

The doping of PCs with fluorescent dyes allows the investigation of the stop-band influence on the photoluminescence properties [28–32]. Near the stop-band of PCs, light propagates at reduced group velocities due to resonant Bragg scattering, which can enhance luminescence by stimulated emission and amplify the absorption of incident light. Another important aspect that can be studied is the possibility to obtain a random laser effect using the dye doped PCs structures [33,34].

Hybrid materials have been fabricated by incorporation of dye molecules into PCs through an emulsion polymerization process in the case of water soluble chromophores [28,32]. Another strategy consists in the loading of dyes by a swelling and deswelling process of the already synthesized colloids [32,35].

In this study, hybrid materials comprised of PDI and PCs have been obtained by two different methods:

- Soap-free emulsion polymerization of styrene and 2-hydroxyethylmethacrylate in the presence of PDI derivatives, despite poor solubility of the dye in water. The substitution on the bay area (1, 6, 7 and 12 tetrachlorine) and the imide

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functionalization (dipentyl) [24,36] of PDI enhances the solubility in organic solvents, such as styrene, thus making possible the polymerization process, but allows significant dye molecule π - π stacking interaction to take place.

- Impregnation of PCs with a PDI solution. The characteristics of solubility of this PDI derivative appeared particularly suitable, making possible the impregnation method without disturbing the crystal arrangement of PCs.

This study aims to investigate the influence of the PDI functionalization on the polymerization process, and the properties of the doped hybrid materials. Thus, the obtained materials have been characterized by DLS, optical microscopy, UV-vis and fluorescence spectroscopy.

2. Materials and methods

2.1. Materials

Styrene (ST) (Merck) has been purified through vacuum distillation. 2-hydroxyethylmethacrylate (HEMA) (Aldrich) has been passed through separation columns filled with Al_2O_3 to remove inhibitors. Potassium persulfate (KPS) (Merck) has been recrystallized from an ethanol/water mixture and then vacuum dried. Perylene-3,4,9,10-tetracarboxylic diimides (N,N'-bis(2'-hydroxyethyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-bis(dicarboximide) PDI 1 and N,N'-dipentyl-1,6,7,12-tetrachloroperylene-3,4:9,10-bis(dicarboximide) PDI 2) were obtained according to previous methods [37,38]. The structures of the chromophores are presented in Scheme 1.

2.2. Methods

2.2.1. Soap-free emulsion polymerization

- *Preparation of the poly(styrene-co-2-hydroxyethylmethacrylate) ST-HEMA colloidal dispersion:* ST (6.5 mL) and HEMA (2 mL) have been added in 100 mL of distilled water together with 62.5 mg of KPS. The reaction mixture has been nitrogen purged and then maintained for 8 h at 75 °C under continuous stirring. The final dispersion has been dialyzed in distilled water for 7 days, using cellulose dialysis membranes (molecular weight cutoff: 12,000–14,000) to remove the unreacted monomer and initiator.
- *Preparation of the ST-HEMA-PDI colloidal dispersions:* A mixture of 6.5 mL of ST and 0.11 g of PDI were added to 100 mL of distilled water containing 62.5 mg of KPS and 2 mL of HEMA. 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 cutoff: 12,000–14,000), in order to remove the unreacted monomers and initiator.
- *Preparation of the PDI films:* 10^{-2} mol L⁻¹ solutions of PDI in chloroform were prepared, and the PDI was deposited on a glass substrate by dip-coating method.
- *Preparation of ST-HEMA + PDI impregnation films:* ST-HEMA film with synthetic opal properties was obtained by gravitational sedimentation on a glass substrate and dried at 70 °C for 1 h. PDI solutions in toluene (10^{-2} mol L⁻¹) were deposited on ST-HEMA surface by dip-coating method.

2.3. Characterization

The particle size measurement, through dynamic light scattering (DLS), and the Z potential were obtained with a Nani ZS device (red badge). 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 recorded using a FP-6500 Jasco spectrofluorometer.

3. Results and discussion

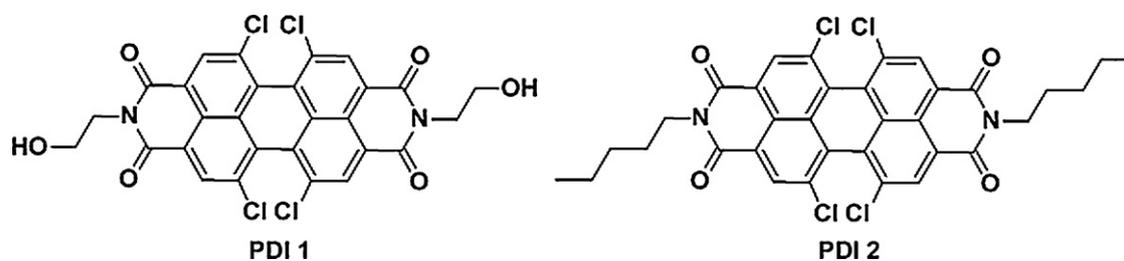
The first stage of this study consists in the determination of the influence of PDI derivatives chromophores (PDI 1 and PDI 2) on the soap-free emulsion copolymerization reaction of ST-HEMA system. Thus, in order to obtain information on the particle dimension and the stability of the latexes, the obtained emulsions were investigated by DLS analysis. The measurements were performed on highly diluted samples in order to rule out interaction and multiple scattering effects. DLS measures Brownian movement according to the particles size. These analyses are obtained by irradiations of the polymer particles with a laser beam and computing the intensity of the scattered light at 90° angles. The results are presented in Fig. 1.

The first information obtained from this analysis was the monodispersity of the obtained systems. The particles dimensions were found to be influenced by the presence of the two PDI derivatives, which leads to a size decrease of the copolymer particles. Thus, for the ST-HEMA the particles size was determined to be 278 nm, for ST-HEMA-PDI 1 system the particles size was 260 nm and for the ST-HEMA-PDI 2 system 269 nm. The particle size variation may be due to the scavenger capability of PDI during the soap-free emulsion polymerization process. In our previous studies, this effect was observed during the polymerization reaction in the presence of fullerene C₆₀. Thus, by homogeneous nucleation, a higher number of particles with smaller dimensions are formed, due to the inhibition in the water phase of the propagating radicals by the PDI molecules transported by the ST from the organic phase. In agreement with our previous investigations [7–9] proving that the majority of hydrophilic groups from the monomer are arranged by homogeneous nucleation at the surface, the PDI moieties should be reasonably arranged inside the copolymer particles. Moreover, the slight difference between the particle size dimension for ST-HEMA-PDI 1 and ST-HEMA-PDI 2 is in accordance with the hydrophilic characteristic of the molecule. A more hydrophilic PDI 1 results in lower particle size, the PDI 1 presenting an increased interaction at the interface with the water phase and thus an increased radical scavenger effect. The values of the Zeta potential for the obtained latexes ST-HEMA, ST-HEMA-PDI 1 and ST-HEMA-PDI 2 (see Fig. 1) were -39 mV, -39.8 mV and -41 mV, respectively, which confirm colloidal stability in all cases.

In order to study the properties of the obtained photonic crystals and due to the particle monodispersity, the next characterization performed was optical microscopy (Fig. 2). The average distance between the defects (resulted from water evaporation) was estimated to 50 μm proving the good quality of the final opal films.

According to Bragg's law, the existence of crystalline structures, will determine the reflection of light at a specific wavelength radiation from the material. Thus, the photonic crystals film presented in Fig. 2 were characterized by UV-vis, using a UV-vis spectrometer equipped with a reflection integration sphere (Fig. 3).

The characteristic peak (stop band) confirms the presence of a crystalline, photonic crystal structure in all three systems. The stop band value is dependent on the size of the particles, which modify the Bragg diffraction of the (1 1 1) planes of the crystalline structure [6,10]. Thus, a blue shift of the stop band is noticed in correlation with a decrease in particle size. Therefore, the UV-vis spectra confirm the data provided by the DLS analysis, proving the obtaining of different data size monodisperse particles with self-assembling capabilities.



Scheme 1. The structures of the chromophores *N,N'*-bis(2'-hydroxyethyl)-1,6,7,12-tetrachloroerylene-3,4:9,10-bis(dicarboximide) (PDI 1) and *N,N'*-dipentyl-1,6,7,12-tetrachloroerylene-3,4:9,10-bis-(dicarboximide) (PDI 2).

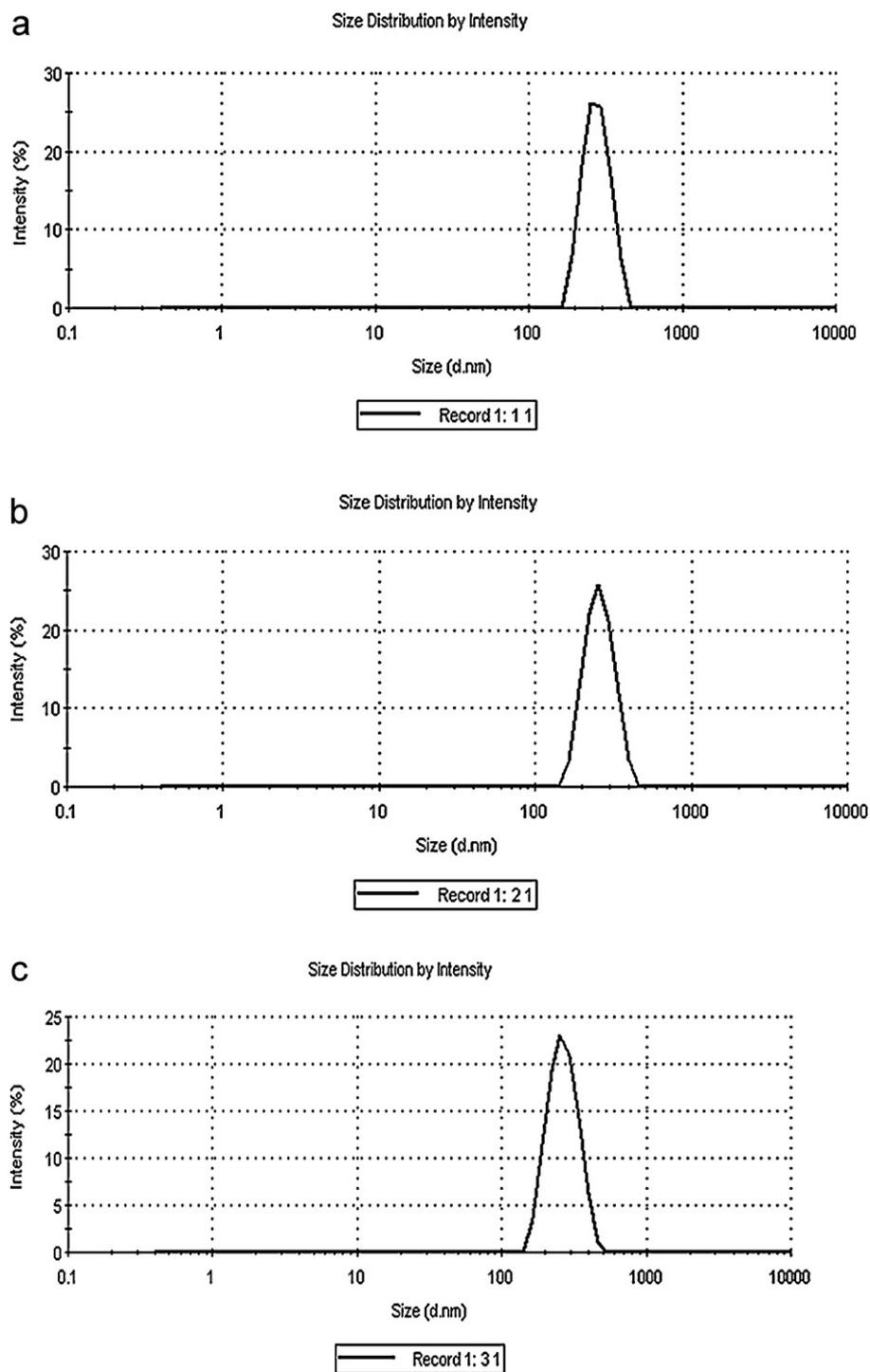


Fig. 1. DLS analysis of: (a) ST-HEMA; (b) ST-HEMA-PDI 1; (c) ST-HEMA-PDI 2 latexes.



Fig. 2. Optical microscope images at various magnifications; from left to right: 20 \times ; 50 \times ; 100 \times for: (a) ST-HEMA; (b) ST-HEMA-PDI 1; (c) ST-HEMA-PDI 2.

For the PDI polymeric films (Fig. 3), a decrease in the reflection response in the absorption domain of PDI is not observed. This can be explained by the incorporation of PDI (scavenger) in the particles and the overlay of the absorption domain and the stop band of the PC. Consequently, the influence of the adsorption band corresponding to free dye is not observed due to the core-shell structure of the hybrid material obtained. All the dye molecules have been incorporated in the polymer particles.

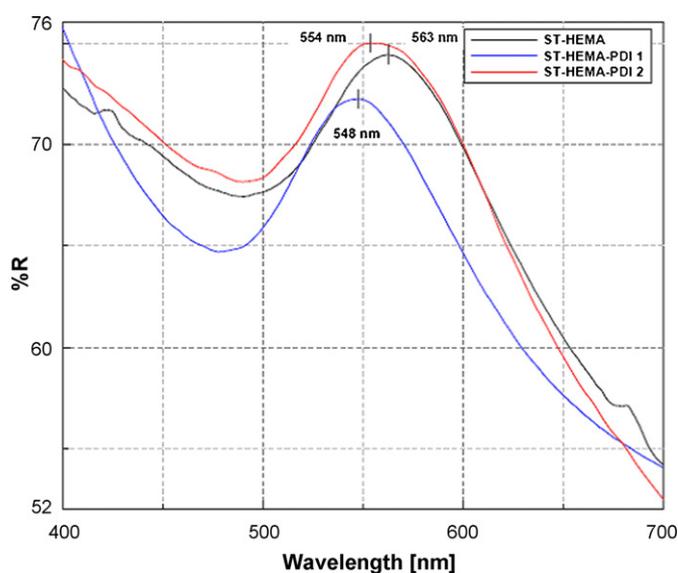


Fig. 3. UV-vis spectra for the polymeric films.

In other works published by our group [39,40], it was demonstrated that in the case of the ST-HEMA core-shell structure is obtained, with the shell composed mainly of HEMA. Therefore, the structures obtained in the presence of PDI can resemble the one presented in Fig. 4.

According to previous articles [31] the photonic crystal may act as a Bragg mirror and can effectively increase fluorescence intensity of organic dyes because of the enhanced excitation and/or emission light. A condition for fluorescence enhancement is that the excitation wavelength is in the stop band of the photonic crystal. The excitation light reflected by a Bragg mirror can stimulate more dye molecules, which also favors fluorescence enhancement. The properties of the hybrid material were studied by comparison with hybrid materials obtained by impregnation of films with chromophore solutions. In both cases an increase of the fluorescence response was observed. In addition, a blue shift for the PDI core particles was also observed, proving the incorporation of the dye inside the copolymer particles.

Considering our previous research [41], we consider relevant the impregnation of the obtained photonic crystals films with PDI solutions and the analysis in comparison of the optical properties.

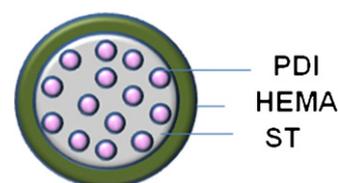


Fig. 4. The core-shell structure of the polymer particles.

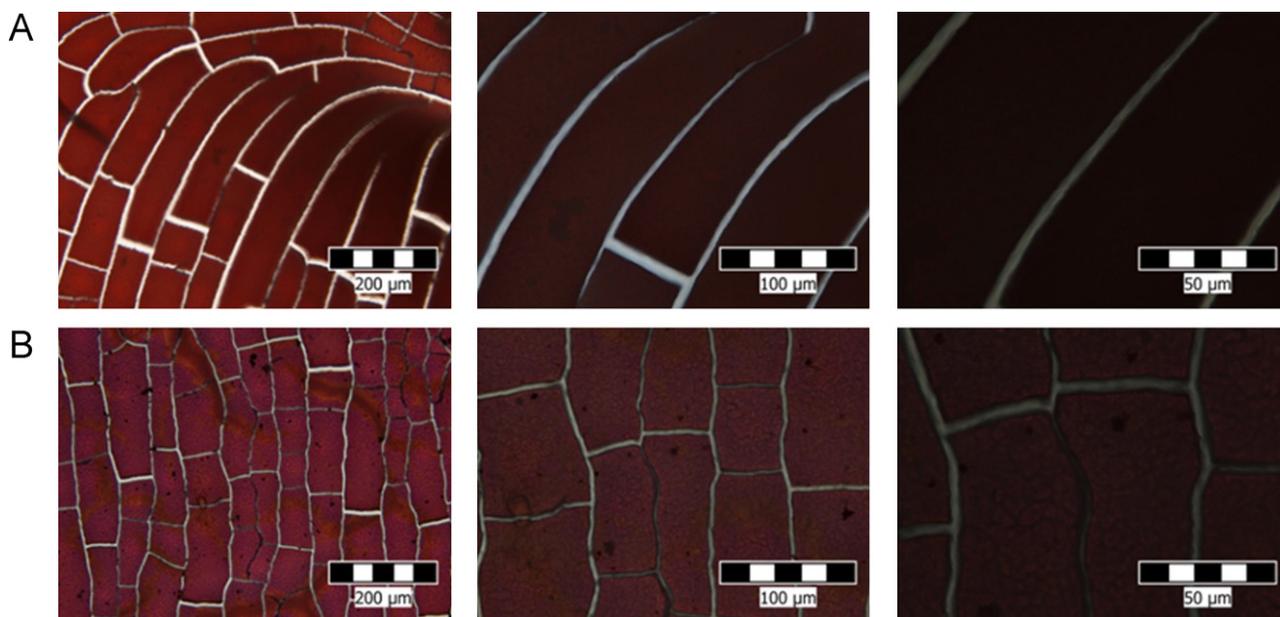


Fig. 5. Optical microscope images at various magnifications; from left to right: 20 \times ; 50 \times ; 100 \times for: (a) ST-HEMA impregnated with PDI 1; (b) ST-HEMA impregnated with PDI 2.

The optical microscopy images for films obtained by impregnation are presented in Fig. 5. Obviously, the presence on the surface of the chromophores, a stronger coloring of the films is observed compared to Fig. 2. In this case, the distances between the defects are 50 μm , confirming that a good photonic crystal structure was obtained and maintained.

Fluorescence spectroscopy was utilized in order to ascertain the incorporation of the chromophore inside the polymer particles and to determine the emission characteristics (Fig. 6).

For both chromophores used in the soap-free emulsion polymerization, investigations were carried out on: (1) the film obtained by water evaporation from the latex obtained in the presence of the chromophores (ST-HEMA-PDI film); (2) the films impregnated with the chromophores (ST-HEMA + PDI film impregnation); (3) the chromophores films deposited on glass (PDI film); (4) the latex from the polymerization reaction (ST-HEMA-PDI latex); (5) the chromophore solution (PDI solution) using an excitation wavelength of 485 nm. A preliminary analysis of the emission characteristics reveals similar responses for PDI 1 and PDI 2 systems. Thus, the response for PDI film is recorded at 575 nm, followed by the ST-HEMA + PDI film impregnation at 560 nm, respectively ST-HEMA-PDI latex, PDI solution and ST-HEMA-PDI film at around 500 nm. These values can only be explained by different physical interaction between the chromophore molecules. Thus, a blue-shift of the emission is noticed with the decrease of size of chromophore aggregates formed (from excimer to individual molecule, respectively monomeric forms) [18,38]. This statement is supported by the emission of PDI solution ($10^{-6} \text{ mol L}^{-1}$) which contains the solvated PDI dye molecules (monomeric form) (500 nm) unlike the films where the physical interaction between the molecules are intense and numerous (leading to excimer's formation) (575 nm). Also, different emission values for the ST-HEMA + PDI impregnation films and PDI films compared to the monomeric emission suggest a different degree of aggregation in these samples. The most important observation is that ST-HEMA-PDI polymer nanoparticles present monomer type emission, which can be explained by the fact that the process of incorporation of the dye molecules inside de polymer particles also acts as impediment in the forming of dye aggregates.

In order study the influence of interaction type between the dye molecules on the fluorescence emission, UV-vis analysis of PDI 2 solution ($7.5 \times 10^{-6} \text{ mol L}^{-1}$), PDI 2 film, ST-HEMA PDI 2 impregnation and PDI 2 solid (Fig. 7) was performed. Both the dye film and the impregnation were realized with a dye solution of $7.5 \times 10^{-6} \text{ mol L}^{-1}$ in toluene. A red shift of PDI 2 characteristic absorption can be noticed in the order: ST-HEMA PDI 2 impregnation < PDI 2 film < PDI 2 solid. This phenomenon can be explained by the aggregates size which can vary in this order from the monomer specie to different size aggregates.

The previous analysis reinforces the fluorescence information, but more interesting would be analysis of the evolution of the interaction between the dye molecules from the start of the polymerization to the final product of the reaction. Thus, the UV-vis spectra of PDI 2 solution (2) in styrene with a concentration equal to the one used in the reaction ($2.25 \times 10^{-4} \text{ mol L}^{-1}$ solution in styrene), PDI 2 solution (1) ($7.5 \times 10^{-6} \text{ mol L}^{-1}$ solution in styrene) and ST-HEMA + PDI 2 impregnation with a solution of $2.25 \times 10^{-4} \text{ mol L}^{-1}$ concentration were recorded. (Fig. 8)

All the examples involve the use of the same dye, a dependence of the absorption characteristics on the concentration of dye used and the interaction arising from this concentration being observed. Thus, a blue-shift of the absorption characteristics is noticed both for the concentrated PDI 2 solution and for photonic crystal impregnated with the more concentrated solution (PDI 2 solution (2)). The self-association of dyes in solution or at the solid-liquid interface is a frequently encountered phenomenon in dye chemistry arising from strong intermolecular Van der Waals-like attractive forces between the molecules, or in our case π - π stacking interaction between perylene bay areas. The aggregates in solution exhibit distinct changes in the absorption band as compared to the monomeric species. Hypsochromic shifts (blue-shifts) are specific to H-aggregates. The H type aggregates are a one-dimensional array of molecules in which the transition moments of individual monomers are aligned parallel to each other and perpendicular to the line joining their centers (face-to-face arrangement). The key point of this study is that at the beginning of the polymerization process the dye molecules are present as H type aggregates, and that by employing a soap-free emulsion polymerization process

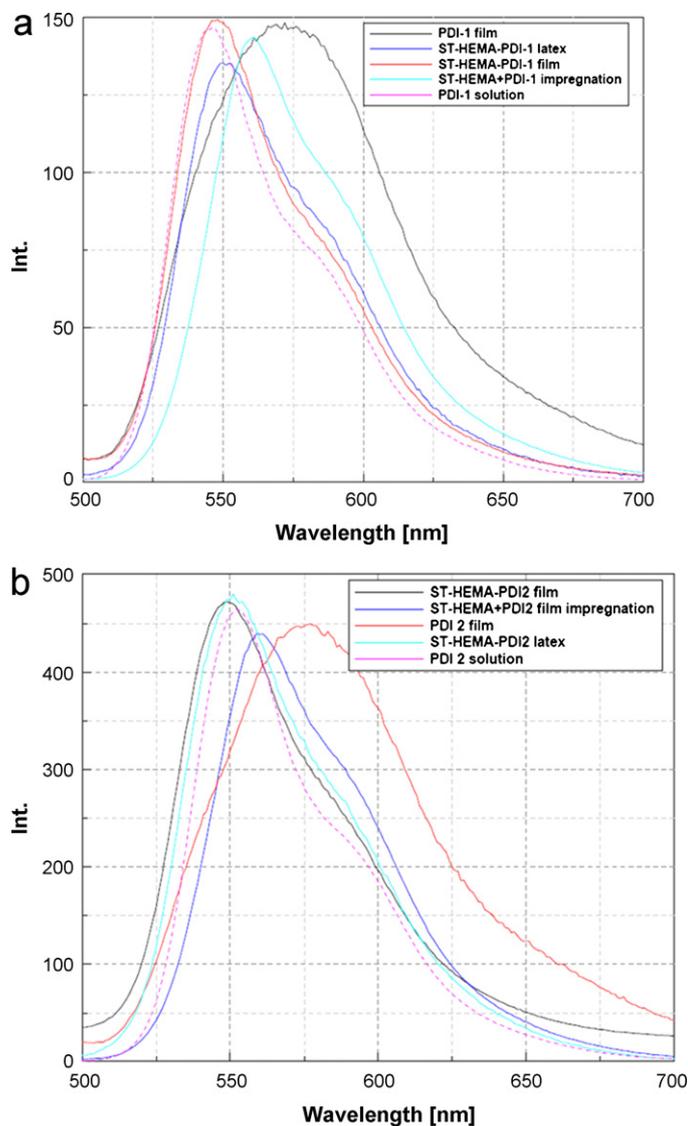


Fig. 6. Fluorescence spectra at an excitation wavelength of 485 nm.

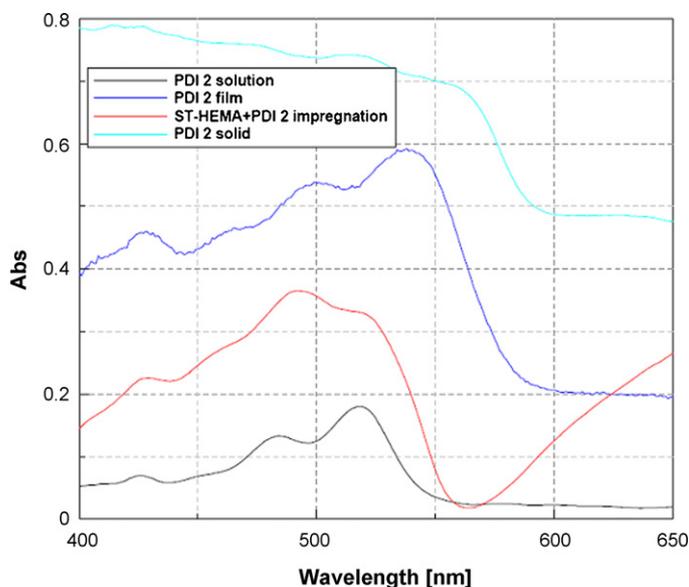


Fig. 7. UV-vis spectra for PDI 2 solution, PDI 2 film, ST-HEMA + PDI 2 impregnation and PDI 2 solid.

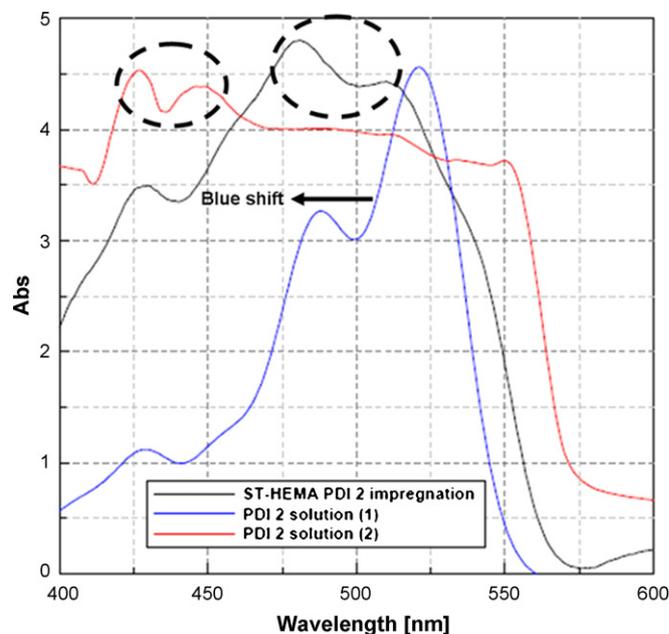


Fig. 8. UV-vis spectra for PDI 2 solution (1), PDI 2 solution (2) and ST-HEMA + PDI 2 impregnation with PDI 2 solution (2).

with the incorporation of dye molecules, in the final material the chromophore molecules are presented as monomer species.

4. Conclusion

Photonic crystals modified with fluorescent chromophores have been obtained by employing soap-free emulsion polymerization in the presence of PDI and by impregnation of the ST-HEMA films with PDI solutions. This study demonstrated that the PDIs influence on the soap-free polymerization of ST-HEMA leads to a decrease in particle size due to its scavenger effect and that the employed method of PDI doping allows the obtaining of monomer type emission of polymer particles containing PDI.

The PCs have been characterized by UV-vis and fluorescence spectroscopy. A blue-shift is noticed with the decrease of size of chromophore aggregates formed (from excimer to individual molecule, respectively monomeric form). This statement is supported by the difference between the emission of PDI solution ($10^{-6} \text{ mol L}^{-1}$) containing the solvated PDI dye molecules (monomeric form) (500 nm) and the films where the physical interaction between the molecules are intense and numerous (leading to excimer's formation) (575 nm).

The key point of this study is that at the beginning of the polymerization process the dye molecules are present as H type aggregates and by employing a soap-free emulsion polymerization process with the incorporation of dye molecules, the final material presents the chromophore molecules as monomer species. This can be explained by the fact that the process of incorporation of the dye molecules inside the polymer particles also acts as impediment in the formation of dye aggregates. Thus, the radical formation and polymer particle nucleation disrupts the dye molecule π - π stacking interaction.

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