Photonic Crystals Band Gap Modulation Using the Pattern of a Written DVD

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This study presents a novel strategy for the modulation of the stop band of a polymer photonic crystal by utilizing the pattern on the surface of a written DVD. Thus, fluorescent dye doped polymer colloids (305 nm) capable to self-assemble have been obtained through soap-free emulsion polymerization and deposited on the surface of the DVD, both the top and bottom. The resulting films were investigated by SEM, UV-Vis and fluorescence spectroscopy. Depending on the design of the surface, the modification of the band gap, as well as the emission properties of the photonic crystals were observed.

Keywords: photonic crystal, band gap, DVD, SEM, fluorescence

Photonic crystals (PCs) [1-4] constitute a fascinating class of materials due to their outstanding interaction and manipulation of light which enables their potential use in a wide range of novel optical devices such as: sensors [5], bioassays [6], colour displays [7], solar energy [8] and lasers [9].

One of the most important characteristics of the photonic crystals is the formation of a stop-band or band-gap [10]. This consists in a range of frequency in which light cannot propagate through the structure. The position and the width of this band are dependent on: the relative refractive index of the self-assembled structure, the lattice constant (distance between the particles or type of crystallization) and particle dimensions [11]. Therefore, one simplest strategy for controlling the band-gap position is the manipulation of the particle size; usually an increase in size leading to a bathochromic shift (red-shift) whereas a decrease leads to a hypsochromic shift (blue-shift) [1]. However, there are examples in the literature where an increase in particle size causes a blue-shift explained by the modification of either the relative refractive index or lattice constant (filling factor) [12].

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 [13]. Also, due to their outstanding photophysical and photochemical properties characterized by high quantum yield of photoluminescence close to the unity, PDI derivatives represent one of the most widely studied classes of organic semiconductors with potential applications as fluorescent dyes [14], near-IR dyes [15], optical and molecular switches [16, 17], artificial photosynthetic systems [18] or molecular wires [19], photosensitizers [20, 21] and as lasers dye [22].

Our previous published work [23] put into evidence the obtaining of PDI doped polymer photonic crystals exhibiting monomer emission.

The aim of this study consists in the modulation of the band-gap position using a patterned support for the self-assembly process of the PDI doped polymer colloids. This consists in a DVD polycarbonate surface presenting a template characteristic to the written information and a refractive index different from the polymer colloids. The deposition of the polymer colloids was realized both on the rough surface (top), as well as on its imprint side (bottom). Furthermore, using polymer colloids doped with a fluorescent dye, it was important to establish the influence of the obtained structures on the optical properties of the materials.

Experimental part

Materials

Styrene (ST) (Merck) has been purified through vacuum distillation. 2-Hydroxyethylacrylate (HEA) has been passed through separation columns filled with Al_2O_3 to remove inhibitors. Potassium persulphate (KPS) (Merck) has been recrystallized from an ethanol/water mixture and then vacuum dried. Perylenediimide (N,N' -Bis(2'-hydroxyethyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-bis(dicarboximide) PDI was obtained according to previous methods [24, 25]. The structure of the chromophore is presented in scheme 1.

Methods

- Preparation of the ST-HEA-PDI colloidal dispersions. A mixture of 5 mL of ST and 0.0185 g of PDI were added to 100 mL of distilled water containing 150 mg of KPS and

Scheme 1. The structure of the chromophore N,N2 -dipentyl-1,6,7,12-tetrachloroperylene-3,4:9,10-bis(dicarboximide) (PDI)

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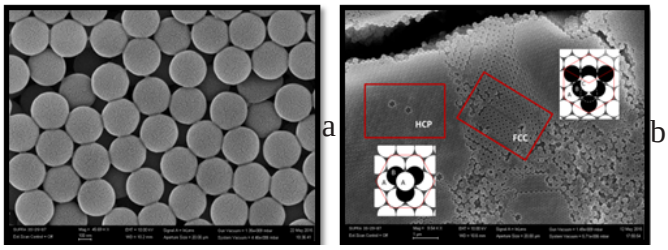

Fig. 1.SEM analysis of the ST-HEA-PDI polymer particles

0.5 mL of HEA. 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 ST-HEA-PDI Films. ST-HEA-PDI film with synthetic opal properties was obtained by gravitational sedimentation on a glass substrate and dried at 70°C for 1 h.

- Preparation of ST-HEA-PDI Films on DVD surface. ST-HEA-PDI films with synthetic opal properties were obtained by gravitational sedimentation on a DVD substrate, dried at 70°C for 1 h.

Characterization

The infrared absorption spectra have been recorded at room temperature with a Nicolet 6700 FTIR spectrometer in the range of 4000–400 cm^{-1}. The UV-VIS spectra were recorded using a V-500 Able Jasco spectrophotometer equipped with an integrating sphere. The fluorescence spectra were registered using a Jasco FP-6500 Able Jasco spectrofluorimeter. For the morphological characterization, scanning electron microscopy analyses were performed using a FE-SEM (field emission scanning electron microscope) RAITH e Line at 10 kV acceleration voltage.

Results and discussions

The first stage of the study consisted in the morphological characterization of the polymer colloids obtained by soap-free emulsion polymerization. In figure 1a, the obtaining of polymer spheres with a diameter around 305 nm are presented. The highly ordered self-assembly of the colloids is confirmed in figure 1b, justifying the obtaining of the photonic crystal structure. The ordering process resulted in two types of crystallization: hexagonal close packed (HCP) as well as face centered cubic (FCC) (fig. 1b). This unusual behavior was presented only in a few published studies [26, 27].

In order to assess the chemical composition of the ST-HEA-PDI polymer particles FTIR analysis was employed. Thus, the characteristic signals for ST (696 cm^{-1} benzene skeletons vibration, 3060 cm^{-1} C-H out of plane deformation occurs and at 1600 cm^{-1} aromatic C-C stretching), for HEA (3266 cm^{-1} O-H vibration peak, 1733 cm^{-1} C=O stretch and 1190 cm^{-1} C–O for ester group) and for PDI (753 cm^{-1} imide ring deformation) are present in figure 2.

The aim of this study consists in the modulation of the band-gap position through the modification of the effective refractive index of the obtained structures, using a novel surface for the self-assembly of the polymer colloids, compared to literature examples [4, 26, 28]. Thus, as support for the polymer colloids the information pattern on a DVD surface was used. The rough surfaces (the top) as well, as the imprint side (bottom) were used for deposition process, allowing different structures to be obtained.

The analysis of the images from figure 3a and 3b (DVD bottom) reveals that the particles tend to arrange in the

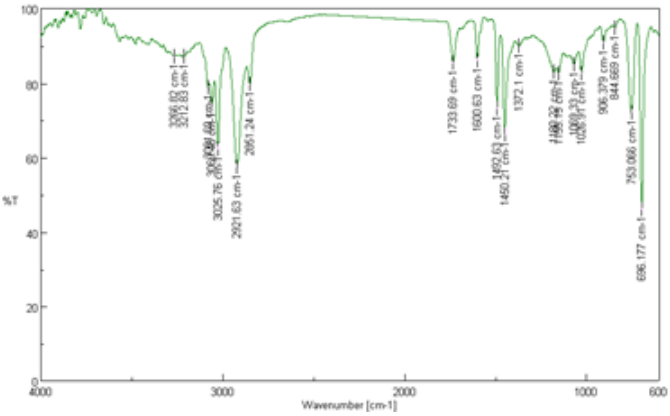

Fig. 2. FTIR spectrum of the ST-HEA-PDI particles

imprinted gaps in contrast with the figure 3c and 3d (DVD top) where the deposition and assembly takes place in the free space around the protuberance, similarly to spheres in a labyrinth.

In order to establish the optical properties of the resulting photonic crystals obtained on the DVD surfaces, UV-Vis spectroscopy was employed.

In figure 4, we can distinguish the band-gap for ST-HEA-PDI on glass at around 740 nm, whereas for the photonic crystals deposited on DVD bottom and upper part it is located at around 670 nm and 570 nm, respectively. Thus, using the same polymer particles, but deposited on different substrates, the position of the band-gap is shifted.

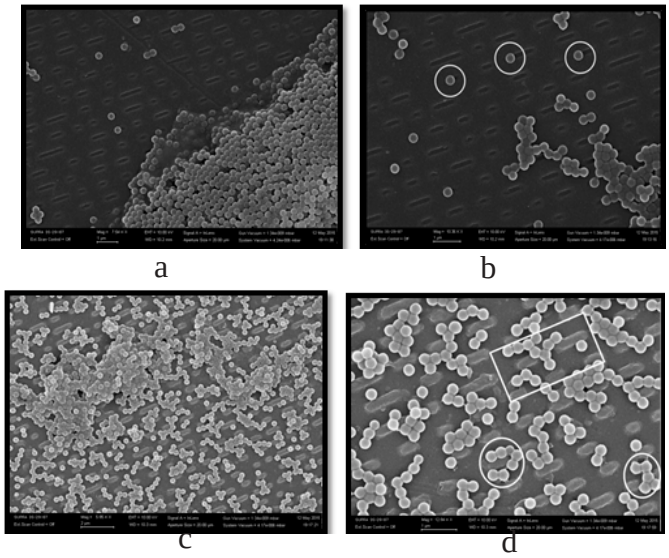

Fig. 3. SEM images of the polymer colloids deposited on the DVD template bottom (a,b) and DVD top (c,d)

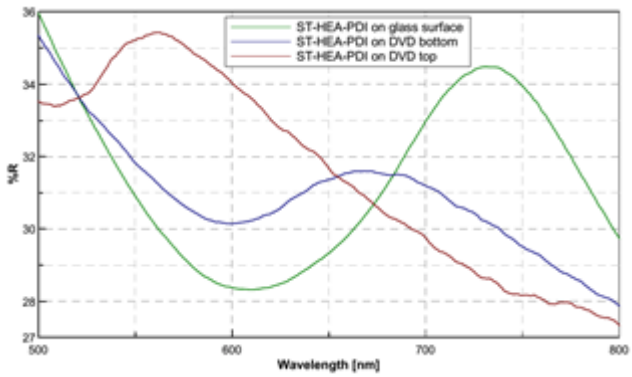

Fig. 4. UV-Vis reflection spectra of the obtained photonic crystals using ST-HEA-PDI polymer colloids on different substrates (glass, DVD bottom, DVD top)

The refractive index of the film (n_{eff}) is dependent by the packing of the structures (*f*-filling factor, which for an ideal

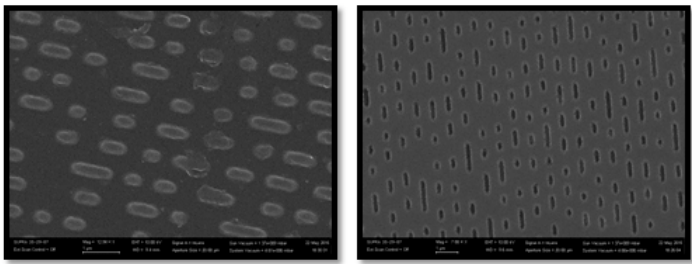

Fig. 5. SEM images of the DVD template top (a) and DVD bottom (b)

face-centered packing is 0.74) and on the refractive index of the constituents.

λ – band-gap wavelength value

$$\lambda = 2 \times n_{eff} \times d \times \sqrt{1 - \frac{1}{n_{eff}^2} \sin^2 \theta} \quad \text{where is} \quad d = \sqrt{\frac{2}{3}} \times D$$

for a FCC packing and θ = incidence angle

$$n_{eff} = f \text{ x } n_{polymer\ colloids} + (1 - f) \text{ x } n_{air}$$

Thus:

$\lambda = n_{eff} \cdot 1.632 \cdot D$, where D – diameter of the polymer colloids (1)

The diameter for the polymer spheres being determined through SEM analysis, the value for n_{eff} can be easily calculated. The obtained value is utilized in equation (2), in order to establish the refractive index of the utilized polymer particles.

$$n_{eff} = f \cdot n_{ST\text{-}HEA\text{-}PDI} + (1\text{-}f) \cdot n_{air} \quad (2)$$

$n_{air} = 1$

$f = 0.74$, the characteristic filling factor specific for a FCC structure [1]

Thus, from the calculation using equations (1) and (2) for the refractive index of ST-HEA-PDI a value of 1.65 was determined. This value is plausible due to the fact that the polymer particles are doped with PDI, the structure of the material being more condensed.

The modification of the n_{eff} value in the two cases (top and bottom) results in a shift of band-gap wavelength value, as determined by UV-Vis analysis. Using equation (1) it is possible to determine the value for the two n_{eff}. Thus, in these cases the structure will contain both, the polymer colloids ST-HEA-PDI, as well as polycarbonate (as the support layer – being not completely covered) and the equation (2) will become:

$$n_{eff1} = f_{1a} \cdot n_{ST\text{-}HEA\text{-}PDI} + f_{2a} \cdot n_{polycarbonate} + (1\text{-}f_{1a}\text{-}f_{2a}) \cdot n_{air} \text{ (top)} \quad (3)$$

and

$$n_{eff2} = f_{1b} \cdot n_{ST\text{-}HEA\text{-}PDI} + f_{2b} \cdot n_{polcarbonate} + (1\text{-}f_{1b}\text{-}f_{2b}) \cdot n_{air} \text{ (bottom)} \quad (4)$$

However, in the equations (3) and (4) the unknown values are f_{1a}, f_{2a}, f_{1b}, si f_{2b}. Thus, using Adobe Photoshop CS5, the proportion of indentations (bottom f_{2b}), respectively protuberances (top f_{2a}) on the DVD surfaces prior to the deposition of the polymer colloids were determined. Therefore, f_{2a} can be approximated to 0.16, while f_{2b} is 0.25 (from the images presented in fig. 5). The data on DVD is encoded by forming pits in the spiral track of the polycarbonate (though the pits appear as ridges from the perspective of the laser). A space between pits is called a *land*. A change from a pit to a land or a land to a pit is a *1* in binary data, while no-change is a *0*.

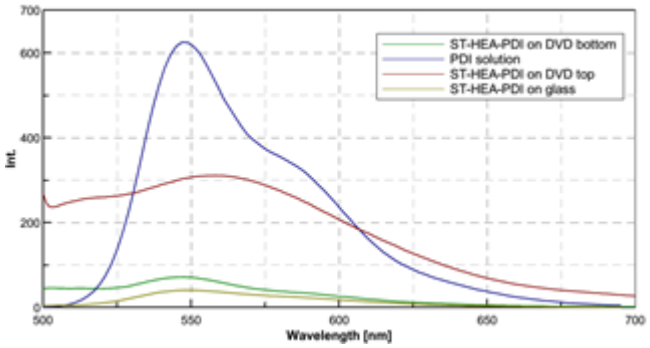

Fig. 6. Fluorescence emission spectra for PDI in solution and the films containing ST-HEA-PDI polymer colloids (excitation wavelength 485 nm)

Considering that the material for both, the top and the bottom is polycarbonate with a refractive index of 1.52 [29], it is possible to determine the value for f_{1a} and f_{1b}. Therefore, for the top surface of 0.023 a filling factor was determined while for the bottom the value was 0.4. These values are in accordance with the SEM images, figure 3 (b and d). Thus, in the case of figure 3c a more pronounced coverage of the surface with polymer colloids compared to figure 3a can be noticed. This aspect can be justified from the perspective of the surfaces morphology which exhibits imprints (cavities) that can be filled with polymer colloids.

In order to investigate the emissive properties of the obtained films, fluorescence spectroscopy was employed. In figure 6 are presented the emission spectra of the materials excited at 485 nm, a wavelength characteristic for the perylenediimide derivative contained in the polymer colloids.

The spectra presented in figure 6, confirm a monomer type emission of the polymer colloids which incorporate PDI [23]. Also, an increase of the emission and a slight red shift can be observed in the case of the ST-HEA colloids assembled on the DVD top surface. This behavior can be explained by the position of the band-gap which leads to an enhancement of the fluorescent properties of the material [23, 30, 31].

Conclusions

The aim of this study consisted in the utilization of the pattern on a DVD surface as support for the self-assembly of polymer colloids particles in order to obtain photonic crystal structures. The influence of the surface design on the assembly process and on the final properties of the materials has been determined by SEM, UV-Vis and fluorescence analysis. Controlling the assembly process and DVD surface choice it is possible to control the band gap position of the obtained films, allowing the realization of blue shifts of the band gap compared to the films deposited on glass surfaces. This modulation was explained through the modification of the effective refractive index of the final structures. The pattern on the DVD surface influences the assembly process of the polymer colloids.

Also, the emissive properties of the films deposited on the DVD surface were determined and found to be enhanced compared to the films deposited on glass surface. Therefore, the band gap modification of the photonic crystal has a positive effect on the optical properties of the obtained materials.

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