Strategies for Dielectric Contrast Enhancement in 1D Planar Polymeric Photonic Crystals

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Abstract: Historically, photonic crystals have been made of inorganic high refractive index materials coupled to air voids to maximize the dielectric contrast and in turn the light confinement. However, these systems are complex, costly, and time-demanding, and the fabrication processes are difficult to scale. Polymer structures promise to tackle this issue thanks to their easy solution and melt processing. Unfortunately, their low dielectric contrast limits their performance. In this work, we propose a concise but exhaustive review of the common polymers employed in the fabrication of planar 1D photonic crystals and new approaches to the enhancement of their dielectric contrast. Transfer matrix method modeling will be employed to quantify the effect of this parameter in standardized structures and to propose a new polymer structure for applications dealing with light management.

Keywords: polymer photonic crystal; dielectric contrast; light management

1. Introduction

Photonic crystals (PhCs) are sub-micrometric dielectric lattices which are widely used in sensing [1–4], waveguiding [5,6], signal switching [7], photovoltaics [8,9], lasing [10], and light management in general [11–13]. In these lattices, the sub-micrometric periodicity of the dielectric function affects photon dynamics in a similar manner to how standard crystalline materials affect electrons. Thus, in analogy with crystalline semiconductors, it is possible to define a photonic band structure with spectral regions that enable photon propagation and forbidden regions, which as a further analogy with semiconductors are called photonic band gaps (PBGs) or stop-bands [14]. The PBGs are detectable by reflectance spectroscopy and generate the typical vivid colors in PhCs [15–18] which are often observed in nature [19–22]. Since their first description in the late 1980s, [23,24] inorganic PhCs made of materials with a large refractive index (e.g., GaAs, GaN, Si) coupled with air voids [25–29] became a paradigm for light control in optoelectronic devices. Inorganic systems provide strong light confinement and outstanding performance. On the other hand, when dealing with large-area applications, the difficulties of reducing costs and scaling-up the fabrications [25–30] has prohibited the use of these materials. To this end, polymeric planar 1D PhCs such as distributed Bragg reflectors (DBRs) and planar microcavities could represent a paradigm changing approach. These structures are easy to fabricate at the laboratory scale via spin-coating [31] or dip-coating [32] and at the very large scale via melt processing with technologies already developed for packaging [33–36].
Unfortunately, polymer DBRs suffer from low dielectric contrast between mutually processable macromolecules—the refractive index contrast ($\Delta n$)—in the transparency region. This characteristic makes them ill-suited for applications requiring accurate light control. In the following paragraphs, we will report on the structures and the characteristics of DBRs fabricated with commercial polymers, focusing on the role of the dielectric contrast. Then, we will review the strategies used to enhance this parameter and employ transfer matrix method modeling to compare the properties of DBRs and microcavities.

2. Background

Figure 1a reports the structure of a DBR. The simple PhC alternates thin films of high and low refractive index materials assembled into a planar 1D lattice, with a periodicity comparable with visible and near infrared wavelengths. When a light beam impinges on this structure, the beam is reflected and refracted (transmitted) by any interface between the two materials. All the beams generated by this process interfere with each other, creating a diffraction pattern in the visible and near-infrared spectral regions that is detectable by means of reflectance or transmittance spectroscopy. When the interference between all the reflected (transmitted) beams is constructive (disruptive), diffraction peaks are detectable in reflectance (transmittance) spectra as maxima (minima). These peaks correspond to the PBG of the structure [14]. Intuitively, the larger the dielectric contrast in the lattice, the more efficient the effect. Figure 1b reports the modelled reflectance response typical for a polymer and an inorganic DBR. Both the structures are made of the same number of layers and have the same layer thicknesses. In detail, the DBRs are made of 15.5 bilayers where the high refractive index (HI) material has a geometric thickness of $d_H = 80$ nm, while the low-index material (LI) has a thickness of $d_L = 110$ nm. The data were modeled using a transfer matrix method (TMM) formalism which has been previously described and is reported in the Supporting Information (SI) [37]. Both the structures show an intense reflectance peak which corresponds to the first-order PBG of the DBRs. The background of both spectra is dominated by a Fabry–Perot interference pattern caused by the partial light reflection at the external surfaces of the crystals. The spectra of the two systems the appear similar in terms of their general features. On the other hand, the PBG of the polymer DBR is blue-shifted, more than 15% less intense and almost four times sharper than the inorganic counterpart. In agreement with the Bragg–Snell law, at normal incidence, the spectral position of the stop-band ($\lambda_{max}$) is a function of the periodicity of the lattice ($d_H + d_L$) and the effective refractive index of the structure ($\lambda_{max} = 2 (d_H + d_L) / n_{eff}$, see SI for details).

![Figure 1](image_url)

**Figure 1.** (a) Schematic of a distributed Bragg reflector (DBR) structure. (b) Typical reflectance spectra for a polymer ($\Delta n = 0.2$, red line) and an inorganic ($\Delta n = 1$, black line) DBR made of 31 alternated layers of low (110 nm) and high (80 nm) refractive index materials.
Figure 1b shows how the larger dielectric contrast typical of inorganics, which easily approaches $\Delta n = 1$, increases the spectral width and the intensity of the PBG with respect to polymers showing lower contrast ($\Delta n = 0.2$ in Figure 1). Indeed, as for other photonic structures, DBRs have been traditionally made of inorganic media with high dielectric contrast by vacuum fabrication methods [38–41] and employed for several applications related to light control, including lasing [42,43], mirrors and filters [44–46], and LEDs [47,48]. Most of these systems, which show a refractive index difference with components larger than $\Delta n = 1$, [49–51], are available commercially [52], but time and cost-demanding fabrications such as sputtering, e-beam evaporations [53,54], or epitaxial vacuum methods [55,56] are required for their production. Furthermore, inorganic multilayers lack flexibility and are usually characterized by poor mechanical properties. Finally, the high temperatures and low pressures used for their fabrication are incompatible with the processing of thin film electronics, which are based on organic materials such as sensitive dyes and emitters [57–59]. Thus, in order to simplify the coupling between DBRs and photoactive materials and reduce costs, a large effort has been dedicated to the development of solution-based fabrication processes. This effort resulted in several new strategies, including the use of polymer solutions and inorganic nanoparticle dispersions for the formation of the DBR building blocks [7,60], and the use of cholesteric liquid crystals [61–63] and block copolymers [64–66]. Currently, amorphous polymer DBRs are the only commercial PhCs available on the square-meter scale [67–71]. However, the relatively small dielectric contrast available for commercial polymers only allows modest effects when dealing with accurate light control applications [37]. Nevertheless, these systems have been proposed in sensing [72–75], emission control [76], and lasing [77].

As mentioned above, solution and melt processing requires the mutual processability of the dielectric components of the lattice, thus limiting the amount of materials suitable for the fabrication and in turn reducing the available dielectric contrast achievable in the transparency region of the polymers. Table 1 lists the polymers commonly employed in DBR fabrication. These are divided into two sub-groups: high refractive index polymers, which are usually soluble in low-polarity organic solvents; and low refractive index polymers, which are soluble in orthogonal solvents with respect to the former type. High-index polymers comprise polystyrene (PS), poly(p-phenylene oxide) (PPO), and poly(N-vinylcarbazole) (PVK). The latter is the commercial polymer with the highest refractive index suitable for DBRs with a PBG in the visible spectral region [37]. Common low-index polymers are poly(acrylic acid) (PAA) and cellulose acetate (CA). The largest dielectric contrast achievable in the visible and near infrared spectral ranges is $\Delta n = 0.21$ for the CA:PVK pair [78–83]. However, PVK is often employed together with PAA [84]. This pairing offers a lower dielectric contrast (i.e., $\Delta n = 0.17$) but very high optical quality DBR structures [85–89]. At times, poly(vinyl alcohol) (PVA) is also reported to be a low refractive index medium [90,91], while recently bio-derived polymers such as alginate and cellulose are attracting attention for the fabrication of DBRs [75,92–94]. However, the need to cast these polymers from water solution limits their application. Indeed, the high surface tension of water and the low wettability of high refractive index polymers often hinder their use.

| Polymer | Refractive Index (at 600 nm) | Solvent Ref. |
|---------|----------------------------|--------------|
| HI      |                            |              |
| PVK     | 1.68                       | Toluene, dichlorobenzene [95] |
| PPO     | 1.57                       | Toluene, carbon tetrachloride [96] |
| PS      | 1.57                       | Toluene [81,97] |
| LH      |                            |              |
| PAA     | 1.51                       | 2-Methyl-2-pentanol [98] |
| CA      | 1.46                       | Diacetone alcohol [81,97] |

HI = high refractive index, LI = low refractive index, PVK = poly(N-vinylcarbazole), PPO = poly(p-phenylene oxide), PS = polystyrene, PAA = poly(acrylic acid), CA = cellulose acetate.
The spectral dispersions of the refractive indexes of the commercial polymers mentioned above are reported in Figure S1 of the SI. For all of them, we note that the refractive index is quite constant in the near infrared part of the spectrum, while their value increases through the visible range until they reach their maximum value in the ultraviolet frequencies. We then observe that the dielectric contrast achievable for DBRs based on PS:CA, which is an established and widely reported system, is as low as \( \Delta n = 0.11 \), while the minimum value, \( \Delta n = 0.07 \), is obtained by coupling PS with PAA. As discussed in the next paragraph, these numbers determine the intensity and spectral width of the peaks assigned to the PBG, which, in accordance with the theory [37], increase as the dielectric contrast grows.

3. Strategies for the Enhancement of the Dielectric Contrast

Small differences in the dielectric contrast can provide large effects on the spectral features and thus in the performances of DBRs. Many strategies have been employed to enhance the dielectric contrast in polymer DBRs by lowering or increasing the refractive index of polymer matrices adopting low or high polarizable molecules or fillers. Figure 2 summarizes the refractive index values at a wavelength of 550 nm for components of the polymer DBRs reported in the literature. Figure S2 in the SI reports the entire spectral dispersion of the optical functions together with the reflectance spectra for DBRs built with these materials where available. As mentioned above, the first DBRs were made of PS and CA. This pairing, as evident in Figure 2, allows a dielectric contrast of about \( \Delta n = 0.11 \). Later, several polymers were investigated for DBR fabrication from solution [99]. For instance, PVK substituted PS to increase the dielectric contrast, reaching \( \Delta n = 0.21 \) [100]. For many years, PVK:CA provided the largest dielectric contrast available for DBRs in the visible spectral range [84,89,101]. This pairing has indeed been widely used for lasing [102,103], switches [104], color purity enhancement in lightening devices [83,105], and emission control [106]. More recently, the easy filmability of PAA made it promising for DBR fabrications with PVK. DBRs made of PVK:PAA have been reported for lasing [84], switches [86], and emission control [87]. Recently, perfluorinated polymers (Hy in Figure 2) have been employed as low refractive index media allowing a value of \( \Delta n = 0.35 \) when coupled to PVK [74,107–110]. To the best of our knowledge, this is the largest value available for commercial polymers suitable for DBRs. However, the low wettability of perfluorinated polymers film leads to the requirement of the activation of its surface to cast further polymer layers, complicating the fabrication process [108].

Against this background, a great deal of attention has been paid to the engineering of polymer refractive indexes [111]. Besides PhCs, processable high or low refractive index media with optical transparency are highly desirable for a number of applications including, among others, light-emitting devices for displays [112,113] and antireflective coatings [57,114]. Very low refractive indexes can be obtained by inserting voids and porosity in the polymer bulk [108,115–120]. In contrast, the refractive index can be increased with high filling volumes [109,118] of inorganic nanoparticles [109,121–123] by the addition of a conjugated system with a high density of delocalized electrons or by the introduction of polarizable atoms [116] in the backbone of the polymer chains. A great effort has thus been dedicated to the development of polymers with intrinsic high refractive index values, such as polyimides and thio-derivatives, which report values larger than 1.7 [111,124–126]. Highly halogenated polymers [127] and systems containing phosphor [128–130] display instead values between 1.6 and 1.7. Likewise, hyperbranched polymers with similar refractive index values have often been reported in the literature [131–133].

In this scenario, several investigations have focused on the implementation of such polymers into DBRs with the aim of enhancing light confinement and thus the performances of optical devices. Hyperbranched polysulphide and inverse-vulcanized polymers [134–138] have been investigated in depth. Moreover, a great deal of attention has been paid to polymers loaded with high index nano-loads made of metal-oxides [139–143] and organometallics [144–146]. One of the first examples regards the use of hyperbranched poly(vinyl sulfide) (HBP, see also Figure S2 of the SI) coupled to CA as a low refractive index material. In this case, the HBP was obtained by cross-linking...
Works on loading polymers with TiO₂ may result in high refractive indexes on one side; however, this implies a noticeable absorption spectrum. Notice that the value for CHIPS is reported in [136,169] at 600 nm. The value at 550 nm is therefore expected to be larger. Bars represent the dielectric contrast achieved in published DBR structures for commercial polymers (blue bars) and coupling commercial polymers with engineered polymeric media (green bars). The red bar represents the maximum theoretical dielectric contrast achievable within a polymeric system. The dielectric contrast bars are ordered from left to right by publication date. HBP: hyperbranched poly(vinyl sulfide); Hy: perfluorinated polymers.

Lastly, sulfur-rich polymers obtained by inverse vulcanization have been investigated in detail in the field of NIR applications. Polymeric elemental sulfur cross-linked by molecules bearing two or more vinyl-type moieties allows high refractive indexes on one side; however, this implies a noticeable...
absorption coefficient in the visible part of the spectrum. This approach allows refractive index values larger than 1.9 when divinylbenzene (CHIPS in Figure 2) is employed as a cross-linker, and of 1.83 for a sulfur copolymer with 2,5-diisopropenylthiophene (IVP in Figure 2, see also Figure S2 of the SI) [136,138,169]. As shown in Figure 2, the largest dielectric contrast reported to date is obtained for DBRs made of titania-based nanocomposite materials. In this sense, coupling these nanocomposites to perfluorinated polymers could lead to a dielectric contrast as large as Δn = 0.64 in the visible range (red bar in Figure 2), making polymer structures competitive with inorganic structures.

4. Role of the Dielectric Contrast in DBRs

Because of the different architectures of the structures mentioned in the previous paragraph, they are hardly comparable in terms of their performances. Thus, we will try to quantify the effect of the dielectric contrast by modeling the optical response for a single architecture (see the SI for details). Figure 3a shows the calculated reflectance spectra for DBRs composed of 15.5 periods. For all the modeled structures, the low refractive index medium has a thickness of d_{L} = 120 nm, while the high refractive index medium has a thickness of d_{H} = 80 nm. Optical functions available from the literature, and reported in Figures S1 and S2 of the SI, were used for both commercial and engineered polymers. Panels b, c and d of Figure 3 compare the figures of merit of this analysis: the reflectance intensity of the first-order PBG (b), its full width at half maximum (FWHM, panel c) and its spectral position (λ_{max}, panel d). In more detail, from bottom to top, Figure 3a shows the calculated spectra for increasing Δn values for PS:CA (black line and dots) [168], PAA:PVK (red line and dots) [91,98], CA:PVK (green line and dots) [106], CA:HBP (blue line and dots) [134], PAA:IVP (cyan line and dots) [138], Hy:PVK (magenta line and dots) [110], CA:TiO_{2}-PVA (yellow line and dots) [170], and Hy:TiO_{2}-PVA (orange line and dots). In general, all reflectance spectra are characterized by an intense peak in the spectral range between 500 and 700 nm. This peak is assigned to the first-order PBG of the structure. The backgrounds display instead a Fabry–Perot pattern due to the entire structure. The intensity and spectral width of the PBG increase with the dielectric contrast, from the bottom spectrum to the top one. It is indeed well-known that the PBG intensity increases linearly with the dielectric contrast and exponentially with the number of periods composing the structure until unitary reflectance [37]. Figure 3b reports the reflectance intensity at λ_{max} for the DBRs versus the dielectric contrast. For the analyzed structure, unitary reflectance is obtained with a dielectric contrast of Δn ≥ 0.3; that is, for the polymer couples PAA:IVP, Hy:PVK, CA:TiO_{2}-PVA and Hy:TiO_{2}-PVA. On the other hand, the exponential dependence of the reflectance intensity on the number of periods allows unitary reflectance also to be reached with a lower dielectric contrast, employing a larger number of layers [37]. Regarding the width of the PBG, Figure 3c shows that it increases linearly with Δn [37]. Indeed, for the lower value corresponding to PS:CA, it approached 44 nm, while it reached 150 nm for the Hy:TiO_{2}-PVA structure. This value is competitive with those obtained for inorganic multilayers fabricated by vacuum technologies [171,172] and with those of mesoporous metal oxide particles fabricated by spin-coating deposition [173–176].

Concerning the spectral position of the PBG, Figure 3a shows that there is no simple correlation to the dielectric contrast. Indeed, the spectra show that λ_{max} tends to red shift for Δn values between 0.11 (PS:CA bottom spectrum) and 0.3 (PAA:IVP, orange spectrum). Then, for Hy:PVK DBR (magenta spectrum), λ_{max} shifts to the blue part of the spectrum with respect to the PAA:IVP structure (cyan line). In fact, λ_{max} depends on the effective refractive index of the DBRs, and then on the refractive index value of both media composing the DBRs averaged regarding the thickness of the layers (see the SI for details). Indeed, λ_{max} moves to the short-wavelength side of the spectrum when a low-index perfluorinated polymer is inserted in the DBR structure as a low refractive index component. This increases Δn on one side and decreases n_{eff} on the other. This effect is clearly visible in Figure 3c, where the spectral position of the PBG is plotted versus the effective refractive index of the investigated structures. In the figure, we can observe that the lowest λ_{max} value corresponds to the Hy:PVK DBR, while the largest value corresponds to the CA:TiO_{2}-PVA DBR.
In the previous paragraph, we have tried to assess the possibility of obtaining strong light confinement with polymer microcavities. This minimum corresponds to the cavity mode and allows photon propagation within the structure. A schematic of a planar microcavity is illustrated in Figure 4a. Its reflectance spectrum is similar to that of DBRs, but a minimum of reflectance within the PBG arises owing to the presence of the defect layer. This minimum corresponds to the cavity mode and allows photon propagation.

These results confirm that DBRs fabricated with polymer media with an engineered refractive index show rather large and intense PBGs. To date, these structures have not been investigated for applications requiring accurate light control. On the other hand, as discussed previously, the dielectric index show rather large and intense PBGs. To date, these structures have not been investigated for other applications requiring accurate light control. On the other hand, as discussed previously, the dielectric contrast that characterizes them is competitive with inorganic DBRs and microcavities. In the next paragraph, we will try to assess the possibility of obtaining strong light confinement with polymer structures through the comparison with inorganic microcavities in which the effect was demonstrated.

5. Prospects for Polymer Planar Microcavities

As mentioned above, the research literature does not report any use of the engineered polymers described in the previous paragraph for the fabrication of microcavities. This might be related to the large number of periods needed to maximize light confinement and to achieve lasing or spontaneous emission rate enhancement together with the processability of the new polymer systems, which is often not optimized. On the other hand, lasing and emission rate enhancement represent the main reason why high dielectric contrast is highly desired in planar PhCs.

One-dimensional microcavities (MC) are structures similar to DBRs in which a "defect" layer is engineered to propagate photons at certain frequencies within the PBG [87,177–179]. The defect layer consists of a thin film with different optical thickness (n × d) with respect to the others composing the structure. A schematic of a planar microcavity is illustrated in Figure 4a. Its reflectance spectrum is similar to that of DBRs, but a minimum of reflectance within the PBG arises owing to the presence of the defect layer. This minimum corresponds to the cavity mode and allows photon propagation.
which is otherwise forbidden for the PBG frequencies. Figure 4b reports the spectra calculated for PS:CA (black line) and Hy:TiO$_2$-PVA (red line) microcavities normalized to the spectral position of the cavity mode ($\lambda_{MC}$). Notice that the spectral position of the defect mode within the PBG and the number of cavity modes depend on the symmetry of the photonic structure as well as on the optical thickness of the cavity layer [11,33,37,85,106]. The spectra were obtained for a defect layer with a thickness of $d_D = 40$ nm and refractive index of $n_{MC} = 1.5$ sandwiched between two DBRs made of 15.5 periods with $d_L = 120$ nm and $d_H = 80$ nm (i.e., the structures discussed in Figure 3). As discussed in the previous paragraph, the intensity and the spectral width of the PBGs increase with the dielectric contrast of the media composing the two DBRs. Concerning the cavity mode centered at $\lambda/\lambda_{MC} = 1$, it is sharper for the structure made with the polymer pairing with a larger $\Delta n$.

![Schematic of a planar microcavity structure](image.png)

**Figure 4.** (a) Schematic of a planar microcavity structure. (b) Calculated reflectance spectra for a PS:CA (black line, $\Delta n = 0.11$) and a Hy:TiO$_2$-PVA (red line, $\Delta n = 0.58$) microcavity of two DBRs composed of 31 alternated layers with thicknesses of $d_L = 120$ nm and $d_H = 80$ nm. The defect layer has a thickness of $d_D = 40$ nm and refractive index of $n_{MC} = 1.5$.

Sharper and deeper cavity modes are symptomatic of the stronger redistribution of the local density of photonic states (LPDOS) and tighter light confinement [37,180–183]. These two parameters play a key role in lasing action and emission rate enhancement [181]. When an emitter is physically positioned in the defect layer and its luminescence spectrum overlaps the microcavity PBG, its emission amplitude is spectrally redistributed by the LPDOS, which is ideally zero at the PBG and infinite at the cavity mode. In real microcavities, the LPDOS is often larger than zero at the PBG and only enhanced at the cavity mode. The LPDOS redistributes the dye emission, which is suppressed at the PBG and funneled when the LPDOS is large at the cavity mode [168,184]. If the emitter displays amplified spontaneous emission (ASE; i.e., population inversion induced by external optical excitation) spectrally overlapped to the allowed mode, when the gain related to the inversion of population is larger than losses, lasing occurs. The fluence threshold of this process decreases for an increasing quality factor ($Q = \lambda_{MC}/\Delta \lambda_{MC}$) of the microcavity [185], which scales linearly with LPDOS [37]. Lasing action has been demonstrated for polymer microcavities fabricated by solution [102,186] and melt processing [35,187–190]. Polymeric [84,87,101,191–196] and hybrid [160] structures as well as elastomeric [95,187] and thermal responsive [34] microcavity lasers have been extensively investigated.

The lasing threshold can also be reduced by the radiative rate enhancement of spontaneous emission. Additionally, this effect is particularly promising for increasing LED efficiency [197]. The rate of spontaneous emission can be altered by modifying the dielectric environment of a medium, obtaining strong spatial confinement [198–204]. A tight confinement also leads to strong spectral redistribution, intensity enhancement [168,205,206], and strong directional control [98,106] and intensifies light–matter interactions [14,46,184,207–210]. These effects are particularly effective for small modal volumes of the microcavity and for large ratios between the density of states at $\lambda_{MC}$ and at the PBG (LPDOS$_{MC}$/LPDOS$_{SB}$), which ideally tends to infinity [198–200,202,207–209,211]. In a planar structure, the modal volume can be approximated to the effective length of the MC ($L_{eff}$), depending on
the field penetration into the DBRs at the side of the defect layers, and then on the dielectric contrast among the DBR components. To date, emission rate enhancement (Purcell effect [201,212,213]) has not been observed for polymer microcavities owing to the low dielectric contrast leading to field penetration into the dielectric mirrors [14,98,106,168,214–218]. Moreover, the rate enhancement effect requires emitters with a sharp spectrum. Indeed, if the emission linewidth is spectrally wider than the defect mode, emission suppression at the PBG compensates enhancement effects at the cavity mode, resulting in the lowering of the rate or the rate being unaffected [14,197,214,215].

As mentioned above, the polymers described in the previous paragraph have never been investigated for lasing or radiative rate enhancement. Thus, it is worthwhile to quantify the effect of the enhanced dielectric contrast obtained with the strategies described in Section 3 on the LPDOS and on $L_{\text{eff}}$. The LPDOS can be easily calculated as a function of the Fresnel coefficients of the top and bottom DBRs from Green’s function, as reported in [219]. Conversely, the effective length depends on $\lambda_{\text{MC}}, n_{\text{MC}}, n_{\text{H}},$ and $n_{\ell}$, as described in [37,180] and in the SI. The contour plot of Figure 5a reports the LPDOS as a function of $\Delta n$ and of the wavelength normalized by the value at the cavity mode ($\lambda/\lambda_{\text{MC}}$). The calculation was performed for microcavities made of the same polymer pairs discussed in Figure 3. The defect layer has a thickness of $d_D = 40 \text{ nm}$ and refractive index of $n_{\text{MC}} = 1.5$, and it is embedded in a structure identical to that considered in Figure 4. LPDOS values are reported in false color so that small values are in green-blue shades while larger values are in red shades.

![Figure 5](image_url)

**Figure 5.** Relation between the local density of photonic states (LPDOS) and $\Delta n$. (a) Contour plot of the LPDOS as a function of $\Delta n$ and normalized wavelength ($\lambda/\lambda_{\text{MC}}$). (b) Ratio between the LPDOS at the cavity mode and at the PBG and (c) MC effective length versus $\Delta n$.

Qualitatively, for all structures investigated, the LPDOS is at maximum at the cavity mode ($\lambda/\lambda_{\text{MC}} = 1$, red area). We also notice that the peak corresponding to this enhancement decreases in width with increasing $\Delta n$. At left side of this peak mode ($\lambda/\lambda_{\text{MC}} < 1$, green area), the LPDOS is small until it increases again at $\lambda/\lambda_{\text{MC}}$ values increasing with $\Delta n$, in agreement with the PBG width observed in Figure 3. Indeed, for $\Delta n = 0.11$ (PS:CA), the spectral range in which the LPDOS is low ranges between $0.94 < \lambda/\lambda_{\text{MC}} < 0.98$, and for $\Delta n = 0.58$ (Hy:TiO$_2$-PVA) it ranges between $0.86 < \lambda/\lambda_{\text{MC}} < 0.99$. The LPDOS is also low at ($\lambda/\lambda_{\text{MC}} > 1$). On the other hand, this area is dominated by an oscillation of density, which can be assigned to the presence of an intense Fabry–Perot pattern. To estimate the ratio LPDOS$_{\text{MC}}$/LPDOS$_{\text{SB}}$, we considered the values at $\lambda/\lambda_{\text{MC}} = 1$ and at $\lambda/\lambda_{\text{MC}} = 0.96$ for all the calculated densities. The ratio is reported in Figure 5b and increases exponentially with dielectric contrast. For PS:CA, this ratio approaches 4 and is larger than 700 for Hy:TiO$_2$-PVA. The large effect induced by the tuning of $\Delta n$ is therefore evident.

Concerning the $L_{\text{eff}}$, Figure 5c shows that the modal length decreases exponentially with the value of $\Delta n$ from $\sim 10.5 \mu m$ for PS:CA microcavity to $\sim 2.2 \mu m$ for Hy:TiO$_2$-PVA one. As the entire microcavity
is 6.2 μm wide, we can estimate that, for a dielectric contrast smaller than 0.2, the field is not confined into the structures, while for a large dielectric contrast the confinement is optimized and reaches roughly one-third of the full microcavity length for the largest Δn. This value seems to be competitive with respect to inorganic structures. Indeed, emission rate enhancement has been demonstrated for Er³⁺ placed into Si/SiO₂ cavities (Δn = 2, L_eff = 1 μm) [220] and for bulk GaAs and GaAs quantum wells placed into AlGaAs/AlAs (max Δn = 0.7, L_eff = 1.7 μm) [221,222]. The effective length of these microcavities is comparable to those achievable with new polymer-based structures; we can therefore envisage the suitability of new polymer-based microcavities for the Purcell effect and for low threshold lasing.

Notwithstanding the fact that the polymers reported in this work have not yet been investigated for applications requiring tight light confinement, this study suggests that the approaches undertaken over the last decade pave the way for these applications. To this end, the processability of the engineered polymers should be investigated in detail and optimized to allow multilayers with extended periodicity, aiming at the fabrication of polymer microcavities. Material processing is indeed a key factor in the fabrication of DBR structures [37]. As previously mentioned, spin-coating deposition is widely used as it provides flat interfaces with a roughness below the nanometer scale and good thickness control [31,104,134,168]. Similarly, dip-coating is increasingly investigated for laboratory scale fabrications [109], although other techniques including layer-by-layer deposition [223] and self-assembling of block copolymers have been investigated in recent years [224,225]. All these techniques have been widely reported for commercial polymers, but few manuscripts describe the processability of engineered polymers suitable for the fabrication of polymer DBRs. For instance, as discussed in this work, perfluorinated polymers show refractive indexes as low as 1.33. On the other hand, their low wettability and chemical stability makes physical surface activation necessary to cast other polymers on their surface [107–110,226]. In most cases, plasma treatments are performed to favor the casting of high refractive index layers on these low wettable polymers. However, plasma surface treatments induce a roughness that may lead to scattering phenomena and decrease the optical quality of the DBRs and microcavities [227–231]. Similarly, employing nanocomposites introduces possible particle aggregation, which would again lead to light scattering and the low quality of the DBR [118,121,139,156,232]. These aspects further highlight the importance of processing engineering for the fabrication of DBRs with engineered polymers.

6. Conclusions and Perspectives

This review focuses on the role of the dielectric contrast in polymer planar photonic crystals. The research interest in these systems arises from the necessity of reducing costs and using milder fabrications than those employed for inorganic structures. On the other hand, despite their ease of processing, even at the large scale, and their low cost compared to inorganics, polymeric systems suffer from low dielectric contrast for mutually processable materials. Several new macromolecular media with modified refractive indexes were proposed in the literature, but only a few have been demonstrated to be suitable for the fabrication of DBRs. We reviewed these systems and envisaged a new possible structure with a dielectric contrast close to that in organic media. This structure uses a perfluorinated polymer as a low refractive index medium and a titania-based polymer nanocomposite as a high refractive index counterpart. Spectral response calculations allowed us to compare inorganic systems with materials that were both reported for the fabrication of multilayered structures but not coupled together and to envisage the possibility of employing them in achieving radiative rate enhancement in light-emitting devices, such as lasers and LEDs.

Supplementary Materials: The following are available online at https://susy.mdpi.com/user/manuscripts/displayFile/37fb0c177ebf3219804197b0baae29f7/supplementary, Figure S1: Spectral dispersion of the refractive index of commonly used polymers for the fabrication of DBRs [5–7], Figure S2: (a) Spectral dispersion of the refractive index of engineered polymers and (b) relative spectra reported in the literature normalized by R_max [8–11].
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