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Curriculum: Chemical Sciences and Technology

Elastomers for Photonic Applications

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“La Scienza ci viene sempre raccontata come un insieme di risultati, conquiste e intuizioni, ma non è altro che un metodo che serve a descrivere il mondo in una forma il più possibile aderente alla realtà. Arriva come uno spietato bagno di umiltà e ci dice che siamo pieni di pregiudizi, che commettiamo tanti errori di valutazione, che li commettono anche le macchine e ci dà gli strumenti per farci da parte, aggiustare il tiro e far sì che i dati parlino e raccontino qualcosa di utile, a prescindere da noi.”

“Science is often presented as a collection of results, achievements, and insights, but it is nothing more than a method that helps us describe the world in a way that aligns as closely as possible with reality. It arrives as a ruthless lesson in humility, telling us that we are full of biases, that we make many errors in judgment, that machines make them too, and it gives us the tools to step aside, correct our aim, and let the data speak and tell us something useful, regardless of us.”

Beatrice Mautino

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Thesis Structure

This Thesis is divided into six chapters, each addressing a specific aspect of the research conducted during the PhD.

- **Chapter 1** introduces the fundamental concepts of photonic crystals, with particular emphasis on Distributed Bragg Reflectors and their use as optical sensors, especially in the context of Structural Health Monitoring, which currently represents the principal application of the structures developed in this Thesis. The chapter also provides a brief introduction to planar microcavity architectures and to the materials employed throughout this work.
- In **Chapter 2**, the principles, fabrication strategies, optical characterization methods, and optimization procedures for Stretchable Distributed Bragg Reflectors (DBRs) are described. Beginning with the motivation for introducing mechanical tunability into photonic structures, this chapter explores the choice of materials, multilayer deposition techniques employed, and opto-mechanical behavior of elastomer-based DBRs under strain. Particular attention will be given to how periodicity modulation affects the photonic bandgap and how mechanical deformation can be used to achieve reversible and controllable shifts in the optical response. This chapter lays the foundation for integrating stretchable photonics with responsive molecular systems.
- **Chapter 3** focuses on the design, realization, and optical-mechanical characterization of a dual-response device obtained by combining Stretchable DBRs with Polymer Mechanophores. This hybrid architecture exploits both photonic and molecular mechanisms in response to mechanical stimuli. This chapter explains the rationale behind merging these two platforms, describes the fabrication pathway for integrating mechanophore-functionalized polymers into a photonic multilayer, and reports experimental data demonstrating how mechanical activation results in simultaneous optical modulation and molecular fluorescence changes. The dual-response concept is analyzed qualitatively and quantitatively, highlighting its potential for sensing, smart materials, and mechanochromic devices.
- **Chapter 4** will concentrate on the study, realization, and characterization of two different stretchable planar microcavity structures. This chapter will provide preliminary results aimed at investigating the feasibility and impact of incorporating fluorophores within stretchable microcavities, with particular attention to their optical response, emission properties, and tunability under mechanical deformation.
- **Chapter 5** reports on a related but independent project concerning the fabrication of photonic structures via dip-coating. In this study, a fused deposition modeling (FDM) 3D printer was creatively repurposed and converted into a dip-coater machine. The chapter illustrates how the modified system was used to deposit multilayer photonic films,

highlighting its advantages, limitations, and potential future improvements and demonstrating a practical approach to accessible photonic fabrication technologies.

- **Chapter 6** summarizes the conclusions of the Thesis, drawing together the main results from all previous chapters.
- The **Appendices** are organized as follows. Appendix 1 collects supplementary figures supporting the Materials and Methods sections, providing visual documentation of experimental procedures, fabrication steps, and setups. Appendix 2 is dedicated to the “Photonic Chocolate” science-popularization activity, a hands-on educational demonstration designed to illustrate the behavior of photonic structures through an intuitive and engaging analogy. Finally, Appendix 3 presents a comprehensive summary of all communications, posters, seminars, and publications produced during the PhD.

1. Introduction

My journey in photonics began with my passion for colors. Since childhood, I have been deeply drawn to visual expression, sketching, and painting. This fascination naturally evolved into a love for art history and contemporary art, where I learned to appreciate the aesthetic power of images and the intellectual depth behind every artistic gesture. Over time, I have come to believe that creativity is not confined to the canvas; it is a fundamental tool for scientific progress. During my doctoral studies, this belief became a guiding principle. Working in photonics has, at times, felt like learning a new form of painting, one where the brush is light itself. What first drew me to colors as a child now resonates in the invisible architectures of reflection and diffraction. If there is one lesson that helped me navigate the multiple challenges of research, it is the realization that a researcher is, in many ways, an artist who constantly designs, reimagines, and pursues inventive solutions to complex societal problems.

Creativity, I have found, is not a luxury in science, it is a necessity. Over these three years, my research, and the results it led to, have been mainly driven by the creativity I brought into my scientific work.

In nature, colors can arise through a variety of mechanisms: chemical pigments, optical effects such as scattering, refraction, and interference, or even bioluminescence. Specifically, pigmentary coloration arises from selective light absorption due to electronic transitions in molecules, whereas bioluminescence results from chemical reactions that produce light at specific wavelengths. Structural coloration, on the other hand, arises from the interaction of light with micro- and nanostructures, whether ordered, partially ordered, or layered, as in soap bubbles.^[1, 2] These structures manipulate light through interference, diffraction, and refraction of light beams, producing some of the most vivid and iridescent colors in nature. ^[3] For example, the brilliant blues and greens of peacock feathers originate not from pigments but from microscopic melanin rods arranged in a periodic lattice. ^[4] Similarly, the wings of Morpho butterflies, the feathers of birds, the scales of fish, mollusks, and even certain plant tissues exhibit intense structural coloration derived from ordered arrangements of transparent materials.^[5] Unlike pigment-based coloration, which often produces dull or diffuse tones, structural coloration generates bright, directional, and sometimes iridescent hues, extending even into the ultraviolet and near infrared ranges.^[6] These natural examples highlight how ordered nanoscale architectures act as photonic

materials, paving the way for biomimetic approaches in modern optics.^[7] Structural coloration also underpins natural strategies of mimicry and camouflage, as seen in insects, reptiles, and cephalopods, where the interplay of light with nanoscale structures allows organisms to blend into their surroundings or signal selectively.^[8] The dynamic color changes observed in chameleons are not due to pigments alone but result from specialized skin cells called iridophores, which contain nanoscale layers of guanine crystals.^[9] By modulating the spacing between these crystals, chameleons can actively tune the wavelengths of light that are reflected, producing rapid and reversible color changes. These nanostructures responsible for colors are natural examples of photonic crystals. In addition, chameleon skin contains other structural elements that reflect near-infrared light, helping with thermoregulation without affecting visible coloration.^[10]

1.1. Photonic Crystals

Photonic crystals (PCs) are composite nanostructures characterized by a periodic spatial arrangement of transparent materials with different refractive indices. This periodicity, typically on the scale of hundreds of nanometers, can occur in one-, two-, or three-dimensional structures, resulting in one-, two-, or three-dimensional photonic structures with corresponding variations in the dielectric constant (Figure 1.1).^[11, 12, 13]

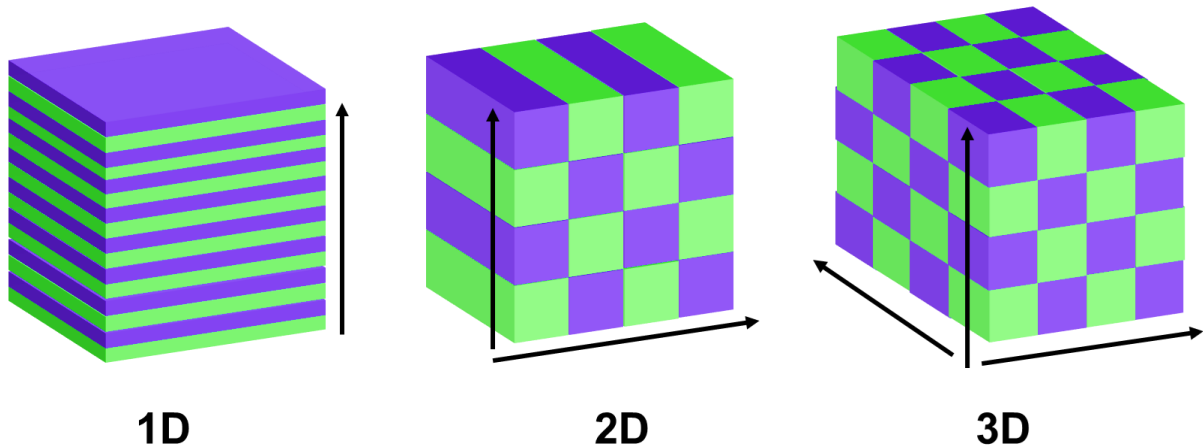


Figure 1.1: Schematic representation of 1D, 2D and 3D Photonic Crystals.

The periodic modulation of the dielectric constant enables PCs to interact with electromagnetic waves in a manner analogous to the diffraction of X-rays by the crystalline lattices. The coherent interaction of light beams reflected and refracted at all the interfaces between the two dielectric materials constituting the PCs leads to destructive or constructive interference. The spectral region

in which light transmission is inhibited owing to destructive interference is known as the Photonic Bandgap (PBG).^[5] Correspondingly, PBGs appear as pronounced reflectance peaks as the interference is there constructive. When the periodicity of the PhC is on the same order of magnitude as the wavelength of visible light, the structure can reflect specific wavelengths, resulting in vivid structural colors. The optical behavior of photonic crystals depends primarily on three factors: the lattice type, periodicity of the structure, and refractive index contrast (Δn) between the constituent materials. By fine-tuning these parameters, it is possible to engineer photonic crystals to manipulate light over a broad spectral range, from near infrared to ultraviolet.^[14] Applications of artificial PCs include low-threshold lasers^[15], enhanced light absorption in photovoltaic devices^[16], optical filters^[17], and highly sensitive chemical^[18] or biological^[19] sensors. Their ability to control and confine light makes them a keystone in the development of modern photonic and optoelectronic devices.

1.2. Distributed Bragg Reflectors

Among the easiest and most extensively investigated configurations of photonic crystals are one-dimensional multilayer structures, commonly referred to as Distributed Bragg Reflectors (DBRs). These systems are composed of alternating layers of materials with high (n_H) and low (n_L) refractive indices, each with respective thicknesses d_H and d_L , which form a periodic sequence of bilayers (Figure 1.2).

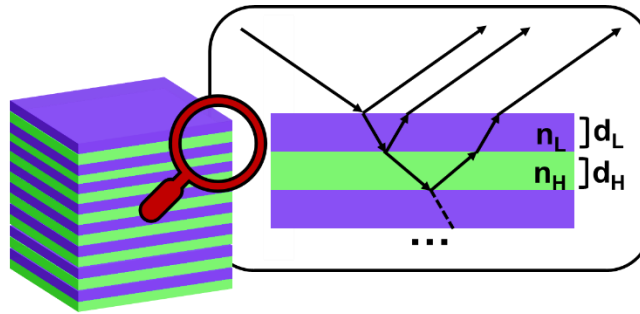


Figure 1.2: Scheme of a DBR with close up to the reflection and transmission of light at each interface.

When electromagnetic radiation impinges on such a multilayer structure at an angle θ_{ext} relative to the surface normal, it undergoes a series of reflections and transmissions at each interface.^[20] Initially, the wave was partially reflected and transmitted at the air–material boundary. The transmitted component propagates through the first layer and reaches the subsequent interface,

where the process is repeated. This sequence continues throughout the stack, assuming that the absorption is negligible. The reflected waves propagate back toward the surface, where they interfere with each other, as do the transmitted waves exiting the structure. Depending on the wavelength, this interference can be constructive or destructive. Constructive interference leads to high reflectivity and the emergence of photonic band gaps (PBGs). The spectral position of the PBG in a DBR can be described by Bragg–Snell’s law (Equation 1.1) ^[21]:

$$m\lambda_{\text{mPBG}} = 2D\sqrt{n_{\text{eff}}^2 - \sin^2\theta_{\text{ext}}} \quad \text{Eq.1.1}$$

where m is an integer representing the diffraction order of the PBG, λ_{mPBG} is the spectral position of the m -order of the PBG, D is the periodicity of the structure ($D=d_L + d_H$), θ_{ext} is the angle of incidence of the light and n_{eff} is the effective refractive index of the materials, that is derived from the volume average of the dielectric functions of the two media ($n^2 = \epsilon$)(Equation 2.2).

$$n_{\text{eff}}^2 = n_h^2 \frac{d_h}{D} + n_l^2 \frac{d_l}{D} \quad \text{Eq. 2.2}$$

The spectral position and intensity of the reflectance peaks associated with the photonic band gaps (PBGs) are governed by several structural parameters, including the thickness of the DBR layers, their refractive indices, and the angle of incidence of the incoming radiation. In addition to the primary PBGs, DBRs typically exhibit interference fringes in the spectral regions surrounding and between the PBGs. These fringes originate from multiple reflections at the top and bottom interfaces of the multilayer stack. In this spectral region, the electromagnetic radiation interacts with the DBR as if it were an effective medium, characterized by an effective refractive index. From the interference pattern, once n_{eff} is known, the total thickness of the structure can be determined. Therefore, these fringes provide valuable information about both the global thickness of the DBR and the optical quality of its external interfaces. Conversely, the appearance of higher-order PBGs is an indicator of the accuracy in the control of layer thicknesses and the absence of defects at the internal interfaces, both crucial aspects for achieving high-performance optical functionality. ^[22]

Figure 1.3 shows an example of the optical response in terms of the reflectance of a DBR and a relative picture showing the vibrant color.

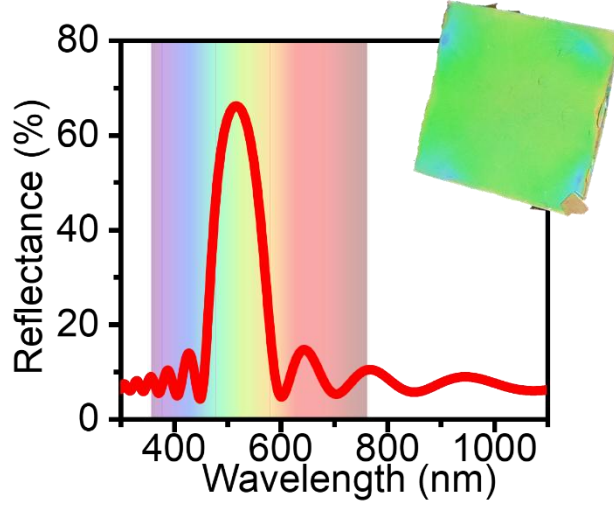


Figure 1.3: Reflectance spectrum and picture of a DBR.

The position of the PBG depends, among the others, also on the polarization of the light impinging on the material (Equation 3a and 3b). ^[20]

$$\text{S - Polarization} \quad \lambda_{\text{PBG}} = 4(d_H + d_L) \frac{n_H n_L \cos \theta_H \cos \theta_L}{n_H \cos \theta_H + n_L \cos \theta_L} \quad \text{Eq. 3.3a}$$

$$\text{P - Polarization} \quad \lambda_{\text{PBG}} = 4 \frac{n_H n_L (d_H \cos^2 \theta_H + d_L \cos^2 \theta_L)}{n_H \cos \theta_L + n_L \cos \theta_H} \quad \text{Eq. 3.3b}$$

When the DBR exhibits refractive index anisotropy along the two polarization directions, a distinct optical response is observed even at normal incidence. In the absence of such anisotropy, as the angle of incidence increases, the wavelength of the PBG shifts toward shorter values for both polarizations. However, the intensity and width of the PBG associated with P-polarized light decrease more significantly as the Brewster angle is approached, whereas those associated with S-polarized light remain almost unchanged. Near the Brewster angle, the overall reflectivity is significantly reduced, thereby preventing the interference effects necessary for the formation of the PBG.

1.3. A way of Modeling the Optical Response of DBRs

The transfer matrix method (TMM) ^[22, 23] is a well-established computational approach for analyzing wave propagation phenomena, and is commonly applied to photons and, in certain cases, to electrons. It remains one of the most widely used techniques for modeling the optical responses of multilayered structures. In this context, the DBR is represented as a sequence of discrete layers, each separated by flat and parallel interfaces. The incident electromagnetic field is decomposed

into a set of plane waves that propagate through the structure and undergo reflection and transmission at each interface. The TMM accounts for all the effects at the interfaces in a simple way enabling accurate simulations of reflectance and transmittance spectra while accounting for polarization effects, finite-size constraints, and wavelength-dependent refractive indices.

1.4. DBRs as Sensors

Among the most promising and widespread applications of polymeric DBRs and PhCs is sensing. The underlying principle is the modulation of the optical response by external stimuli such as chemical analytes or mechanical forces. In polymeric DBRs, analyte molecules can penetrate the structure, inducing swelling in one or both of the polymer layers. This alters the lattice periodicity and effective refractive index, shifting the PBG towards longer wavelengths and producing a visually detectable color change.^[24] In the analogous structures made by mesoporous inorganic materials, swelling is typically negligible because of mechanical rigidity, and optical shifts arise primarily from changes in the effective refractive index upon analyte infiltration. Although the spectral shifts are smaller than those in polymers, inorganic DBRs benefit from a higher dielectric contrast, yielding broader and more intense reflection peaks. The broad applicability of DBR-based sensors is evident in their responsiveness to liquid, vapor, and biological molecules. Polymers offer advantages such as low-cost fabrication, ease of integration into lab-on-a-chip devices, and optical readouts without external power. Tuning the polymer type, layer thickness, and lattice periodicity enables PBGs in the visible range, allowing direct colorimetric detection. The inclusion of functional dyes or fluorophores, such as aggregation-induced emission (AIE) molecules, can further enhance the sensitivity and specificity, providing robust “on/off” signals in response to target analytes. Beyond chemical sensing, DBRs can also function as mechanical sensors for the same reasons.^[25] Mechanochromic DBRs exploit the sensitivity of structural color to strain: stretching or compressing the multilayer alters layer thicknesses and refractive indices, consequently shifting the PBG and producing a visible color change, as shown in Figure 1.4. This enables real-time monitoring of mechanical deformations, with applications in wearable strain sensors, structural health monitoring, and multifunctional devices capable of detecting both chemical and mechanical stimuli.^[26]

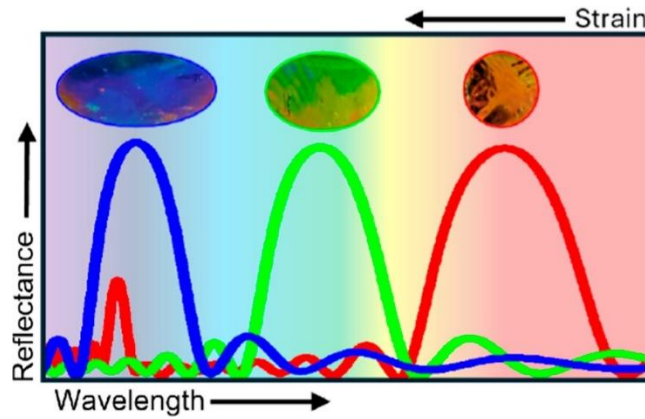


Figure 1.4: Mechanochromism effect of DBRs.

1.5. Structural Health Monitoring

The health of a structure refers to its current ability to safely and effectively deliver its intended level of service while withstanding the anticipated hazards throughout its operational life. In modern engineering, Structural Health Monitoring (SHM) has emerged as a vital discipline focused on ensuring the safety, reliability, and performance of structures across diverse sectors, including aerospace, civil infrastructure, marine systems, energy, and transportation (Figure 1.5).

[27]

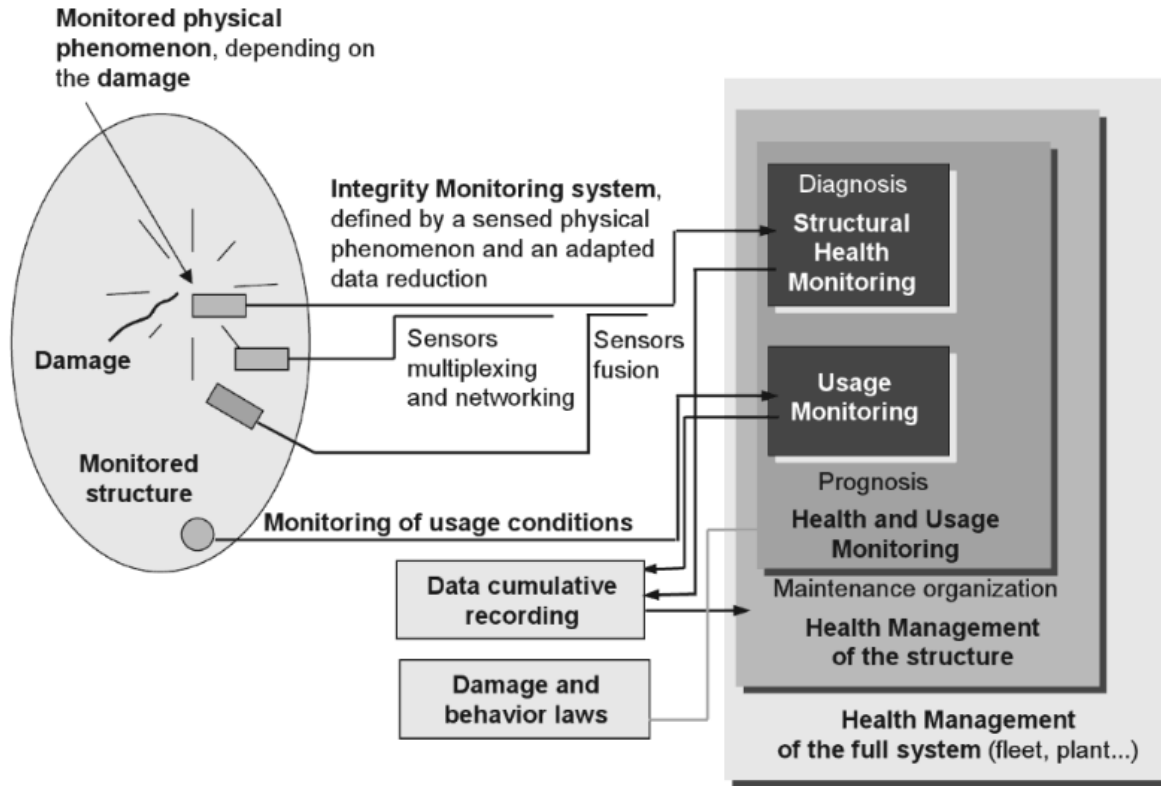


Figure 1.5: Principle of SHM systems.

In civil engineering, SHM is applied to critical infrastructure, such as bridges, buildings, towers, pipelines, tunnels, and dams. ^[28] Although these structures are designed using rigorous engineering standards, they inevitably deteriorate over time owing to factors such as material aging, cyclic loading, and environmental influences, most notably steel corrosion and concrete carbonation. ^[29] Additionally, natural disasters, such as earthquakes, hurricanes, and floods, can accelerate structural degradation. These variables are inherently uncertain, making it difficult to assess the condition of a structure based solely on its age or usage.



Surferside, USA



Tacoma, USA

Figure 1.6: Examples of structural failure. ^[30]

SHM addresses this challenge by employing a network of sensors, integrated hardware, and intelligent software to monitor the response of a structure to external stimuli, either continuously or at regular intervals. Unlike traditional non-destructive evaluation methods, which often require manual inspections and can result in significant downtime, SHM enables autonomous, real-time, in-situ assessments of structural integrity.^[31, 32] This shift enables predictive maintenance strategies, allowing organizations to anticipate structural failures, extend service life, and enhance safety and operational continuity. Unexpected structural collapses can have catastrophic consequences, not only causing economic disruption but also leading to loss of human life and environmental damage. Two examples of structural failures that resulted in significant consequences are shown in Figure 1.6. A tragic and emblematic example that underscores the critical importance of SHM is the collapse of the Morandi Bridge (Polcevera Viaduct) in Genoa, Italy, on August 14, 2018. Being born and raised in Genoa and having witnessed the profound impact of that failure on my community, this event deeply affected me and planted the seed of my interest in SHM. This made me realize how crucial it is to develop technologies that can safeguard lives and prevent such disasters. The bridge, which had been in service for over five decades, served as a vital transportation artery connecting the port of Genoa to major Italian and European destinations. Despite its strategic significance, the structure lacked a comprehensive SHM system capable of detecting early signs of deterioration.^[33] Subsequent investigations revealed severe

degradation in the reinforcement of key cable-stay sections.^[34] Analytical studies employing classical engineering models and finite element simulations indicated that structural failure could have occurred as early as 2014–2016.^[35] These findings strongly suggest that had an SHM system been in place, early warning indicators might have been identified, potentially preventing the disaster. This tragic example highlights the importance of SHM as a cornerstone of modern infrastructure management. The imperative to detect damage at its earliest stage, before compromising structural integrity, has driven significant advancements in SHM technologies. Over the past few decades, the importance of SHM has grown steadily, fueled by increasing societal demands for infrastructure that is not only safer and more resilient but also economically and environmentally sustainable. SHM is based on the principle that any damage within a structure, whether manifested as cracks, delamination, corrosion, or fatigue, alters its physical properties, including stiffness, mass distribution, and damping characteristics.^[36] These changes, in turn, produce measurable variations in the dynamic response, optical signatures, or other observable parameters of the structure. SHM techniques are designed to capture these variations and systematically relate them to the presence and severity of damage.^[37] A wide range of sensing technologies has been developed for structural health monitoring (SHM). Conventional devices, such as electrical strain gauges^[38], fiber-optic sensors^[39], piezoelectric transducers^[40], and accelerometers^[41], remain widely used. Fiber-optic sensors^[39], in particular, offer advantages including multiplexing, immunity to electromagnetic interference, and suitability for long-distance monitoring. More recently, distributed sensing systems have enabled quasi-continuous observation of entire components^[42], while non-contact techniques like digital image correlation and laser Doppler vibrometers allow displacement and vibration measurements without direct sensor integration.^[43] Data collected from these sensors require thorough processing to extract meaningful information about structural integrity. Classical methods, such as frequency-domain and wavelet analyses, help identify damage signatures, while statistical pattern recognition distinguishes normal behavior from anomalies. The integration of machine learning and artificial intelligence has further enhanced automated feature extraction and the early detection of complex damage scenarios.^[44] One of the most significant developments in this context is the digital twin, a virtual model of a structure continuously updated with sensor data to enable real-time monitoring and predictive maintenance.^[45] Despite these advances, SHM still faces key challenges, including the trade-off between sensitivity and robustness, scalability, and cost.^[46] Large infrastructures also

demand extensive sensor networks, generating massive datasets that require advanced analytics, cybersecurity, and significant energy resources.^[47] Emerging materials science offers promising solutions. Self-sensing materials^[36], where the structure itself acts as a sensor, represent a paradigm shift in SHM. Embedding sensing capabilities into construction materials, such as self-monitoring composites^[48] or mechanochromic photonic systems^[49], could transform infrastructure design and maintenance, extending service life, and enhancing sustainability and resilience. The present PhD thesis is situated within this evolving and multidisciplinary landscape. By contributing to the advancement of SHM methodologies and technologies, this study aims to support the development of smarter, safer, and more sustainable infrastructure systems in the future.

1.6. Planar Microcavities

Planar microcavities (MCs) are optical nanostructures characterized by the confinement of light in a defined region between two highly reflective mirrors, typically realized as DBRs. The concept of an MC arises from the fundamental principle of optical interference: when light propagates through a medium with alternating refractive indices, constructive and destructive interference produces spectral regions in which light is either strongly reflected or allowed to propagate. As highlighted in the previous sections, this interference leads to the formation of PBGs, spectral regions in which the propagation of specific wavelengths is prohibited. A MC is formed by introducing an engineered periodicity defect layer between two DBRs, as shown in Figure 1.7. The defect breaks the perfect periodicity of the multilayer stack, creating localized optical modes within the PBG region. These modes, referred to as cavity modes, exhibit narrow linewidths and are highly sensitive to variations in the optical path length of the cavities.^[50, 51] The reflectance spectrum of the MC, shown in Figure 1.7, exhibits a distinct feature compared to that of a conventional DBR: a pronounced minimum within the PBG. While the PBG typically defines the spectral range in which light transmission is inhibited owing to destructive interference, the presence of a reflectance minimum within this region indicates a localized spectral window where light is selectively allowed to propagate through the structure.

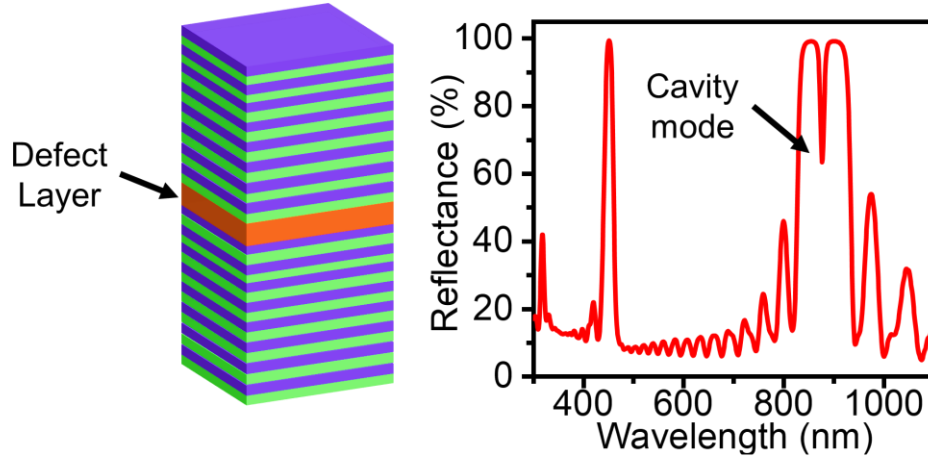


Figure 1.7: Scheme and reflectance spectra of a planar MC.

The optical response of planar MCs is determined not only by geometric parameters but also by material properties, such as refractive index dispersion, absorption, and birefringence. The defect layer plays a central role in defining cavity modes. The refractive index and thickness govern the resonance wavelength, linewidth, and field confinement. By carefully engineering the defect layer, including multilayered or composite designs, spectral selectivity, mode splitting, or enhancement of light-matter interactions can be achieved. Furthermore, embedding active materials, such as fluorescent dyes^[52], quantum dots^[53], or nonlinear optical systems^[54], into the defect layer enables the cavity to serve as a platform for emission control, optical modulation, or nonlinear optical processes.^[55, 56, 57] By precisely controlling the same parameters as those of the DBRs during fabrication, it is possible to engineer the PBG and, in turn, the position of the cavity modes. This precise tunability makes planar MCs ideal for applications ranging from optical filtering and light emission control to nonlinear optics and photonic devices.^[51, 58] One of the key advantages of planar MCs is their ability to enhance light-matter interactions. Within the cavity, the optical field is concentrated in the defect region, which can lead to modified spontaneous emission rates, a phenomenon known as the Purcell effect.^[59] This property has been exploited extensively in photonic devices, including vertical-cavity surface-emitting lasers (VCSELs)^[60], light-emitting diodes^[61] and optical modulators^[56]. The combination of high-quality reflectors and a well-defined defect layer ensures that the cavity can sustain high-Q resonances, which are crucial for achieving strong optical confinement and enhanced performance.^[62]

Planar MCs can be fabricated using both inorganic and organic materials. Inorganic DBRs, typically composed of alternating layers of oxides such as TiO_2 and SiO_2 , offer excellent optical contrast and thermal stability. However, their fabrication often requires vacuum deposition techniques, high temperatures, and precise thickness control, which can increase the complexity and cost. In contrast, polymer-based DBRs offer a versatile and scalable alternative.^[59] Polymers can be solution-processed, spin-coated, or co-extruded to produce multilayer structures with controlled thickness. Additionally, polymeric materials offer the unique possibility of mechanical flexibility, enabling the development of deformable microcavities whose optical properties can be tuned through external stress, strain, or bending.

Mechanically deformable planar MCs represent a new frontier in photonics. When the DBR or defect layers are composed of elastomeric materials, mechanical manipulation modifies both the physical thickness and, in some cases, the refractive index of the layers.^[63] As a result, the PBG and cavity modes shift in response to stretching, compression, or bending. This capability allows for dynamic control over the spectral response of the cavity, opening opportunities for tunable photonic devices, flexible optical elements, and mechano-optical sensors. The interplay between mechanical deformation and optical properties in elastomeric microcavities provides a platform for studying strain-dependent photonic phenomena and designing devices with reconfigurable functionalities.

1.7. Materials selection: Thermoplastic Elastomers

As thermoplastic elastomers (TPEs) were extensively employed in this work, it is appropriate to briefly introduce their main characteristics and their relevance to the adopted fabrication approach. The spin-coating technique, widely utilized in the preparation of multilayered nanostructures as distributed Bragg reflectors^[14] or planar microcavities^[52], requires materials that are processable from solution.^[64] Accordingly, TPEs were selected due to their unique ability to bridge the gap between conventional vulcanized rubbers and thermoplastics. They exhibit rubber-like elasticity under ambient conditions, retaining the soft, elastic properties of conventional rubbers, while also maintaining solubility and melt processability at high temperatures, characteristic of thermoplastics, features that make them particularly suitable for solution-based deposition methods. Structurally, TPEs comprise two distinct, phase-separated components.^[65, 66]

- a soft, amorphous rubbery phase responsible for elasticity;

- a hard thermoplastic phase that provides reversible physical crosslinks.

These hard domains, below their glass transition temperature, act analogously to the chemical crosslinks in conventional rubbers but dissociate upon heating, allowing reprocessing and recycling without degradation and the material can also be dissolved in suitable solvents for solution-based processing.

1.7.1. Styrenic Block Copolymers (TPE-S)

Within the TPE family, styrenic block copolymers are the most widely utilized. The archetypal members, styrene–butadiene–styrene (SBS) and styrene–ethylene/butylene–styrene (SEBS), are synthesized via living anionic polymerization, which enables precise control over the block length and molecular architecture (linear, radial, or star-shaped). For this study, these polymers were specifically selected as representative TPEs, acknowledging that other materials within the broader family could also be explored, but providing a practical starting point for the investigation.

In SBS, polystyrene end blocks ($T_g \approx 100\text{ }^{\circ}\text{C}$) form rigid, glassy microdomains dispersed within a continuous rubbery polybutadiene matrix ($T_g \approx -90\text{ }^{\circ}\text{C}$). This biphasic morphology, confirmed by small-angle X-ray scattering and transmission electron microscopy, yields materials that behave as crosslinked rubbers at room temperature but flow as thermoplastics above the T_g of styrene.^[67]

The hydrogenation of SBS produces SEBS, in which the polybutadiene mid-block is converted to a saturated poly(ethylene–butylene) block. This modification eliminates residual unsaturation, substantially improving the oxidative, UV, and thermal stabilities while retaining the desirable mechanical properties of the parent SBS.^[68]

When modified through grafting with maleic anhydride (MAH), the SEBS elastomer demonstrates enhanced fluidity, temperature resistance, and aging stability. MAH grafting is a widely used modification technique that improves the compatibility of SEBS with other materials and was specifically chosen in this study for the ease with which it can adhere to the other components of the nanostructures. The grafting process, typically initiated by radicals at high temperatures, involves covalent bonding of MAH moieties to the polybutylene segments of SEBS, introducing polar functional groups while largely preserving the polystyrene domains. This chemical modification enhances interfacial interactions with polar materials, improving adhesion to metals, glass, or polar polymers.^[69, 70]

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2. Stretchable Distributed Bragg Reflectors as Strain-Responsive Mechanochromic Sensors

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Chapter at a Glance: Chapter 2 presents the development of elastomeric distributed Bragg reflectors (DBRs) that exhibit mechanochromic responses detectable without the need for complex instrumentation. The structures were fabricated by alternating thin films of a thermoplastic fluoropolymer and a styrene–butadiene copolymer on three distinct elastomeric substrates, allowing the tailoring of both mechanical and optical properties. The resulting DBRs display multiple photonic bandgaps spanning from the visible to the near-infrared spectral regions and demonstrate fully reversible and immediate shifts in response to mechanical strain, with performance maintained over ten deformation cycles at 100% strain. By comparing stress–strain characteristics with optical responses, a mechanochromic sensitivity ranging from approximately 1.7 to 6.9 nm per percent strain, and around 80 nm per MPa, was determined, along with an optical Poisson’s ratio between 0.3 and 0.7, which varies spectrally. Building on this foundation, a second generation of stretchable DBRs was developed using a dynamic spin-coating process and an alternative styrene-based thermoplastic material, achieving improved optical quality and enabling the fabrication of free-standing, substrate-free structures. This work establishes a robust platform for visible, tunable, and reversible mechanochromic photonic devices, highlighting their potential for practical optomechanical sensing applications.

2.1. Introduction

Materials that undergo permanent or reversible color changes when subjected to mechanical stress are attracting considerable interest across multiple fields, including packaging^[1], healthcare^[2] and structural health monitoring^[3]. On the other hand, mechanical stress is also used to modulate optical responses in optoelectronic devices, such as stretchable tunable lasers or nano-optomechanical cavities employed in reconfigurable photonic systems.^[4, 5, 6]

A well-known class of mechanochromic materials includes conjugated polymers like poly(diacetylene), where mechanical stimuli induce conformational changes in the polymer backbone, affecting chain planarization or distortion and consequently altering their absorption

and emission spectra.^[7] Comparable effects are observed in molecules where changes in torsional dihedral angles influence π -electron delocalization.^[8, 9] However, these systems often require high temperatures to provide sufficient polymer chain mobility for sensitive responses. In contrast, supramolecular mechanophores rely on mechanical modulation of intermolecular interactions that affect their fluorescence emission.^[10]

The mechanochromic response can manifest through changes in luminescence, absorption, or light reflection.^[7] While sensors based on fluorescence emission require an external excitation source, systems exhibiting simple color variations are technologically valuable as they enable passive detection without the need for any energy input. Within this framework, PhCs present a highly promising platform for generating easily interpretable, structurally based colorimetric responses. As already discussed in Chapter 1, these structures consist of a periodic modulation of the refractive index on the scale of hundreds of nanometers, which leads to coherent light diffraction and the creation of PBGs, spectral regions where light is strongly reflected.^[11, 12]

Mechanical deformation alters the submicrometric periodicity of these photonic structures, resulting in pronounced color shifts.^[13] This phenomenon is naturally observed in chameleon skin, where mechanical stresses modify the periodicity of guanine nanocrystals arranged in iridophores, forming a photonic crystal with a tunable photonic band gap that enables dynamic camouflage and thermoregulation.^[14]

Regarding synthetic structures, polymer-based PhCs offer significant mechanical advantages such as superior flexibility and Young's modulus compared to inorganic counterparts.^[15, 16] They have demonstrated great potential in multiple applications including sensing^[17], lasing^[18], thermal management^[19], and smart packaging^[20]. Elastomeric polymers, in particular, play a pivotal role in mechanochromic applications due to their low energy and economic costs.^[21] Fabrication techniques such as nanoimprint and colloidal lithography have been extensively employed to create 2D and 3D mechanochromic PhCs.^[22, 23, 24] Nanoimprint lithography has been applied to produce hole arrays in polydimethylsiloxane^[25], while colloidal self-assembly has been used to fabricate 3D structures of silica particles embedded in elastomeric matrices.^[26] Although both approaches yield mechanochromic sensitivity through lattice distortions, nanoimprint lithography involves complex mold fabrication, and achieving large-area, highly ordered 3D PhCs via self-assembly remains challenging. In this context, large-area one-dimensional planar PhCs, known as

DBRs, offer a simpler alternative. Examples of mechanochromic DBRs are scarce in the literature. [22] The use of elastomers at the laboratory scale is often hindered by the insolubility of most cross-linked elastomers and relatively small refractive index contrasts, requiring a large number of layers to achieve bright PBGs and thus making difficult the fabrication process. Among the few reported studies, Howell et al. [27] demonstrated spun-cast DBRs based on a photocurable elastomer doped with ZnO nanoparticles to enhance the refractive index, while Miller et al. [28] proposed a fabrication method inspired by Lippmann photography. Additionally, only limited examples of block copolymer self-assembly for DBRs have been reported. [29] In this chapter, we propose a rapid fabrication method that bypasses the need for cross-linking by using two soluble thermoplastic elastomers. DBRs are fabricated by alternating layers of styrene–butadiene copolymer, serving as the high refractive index component, and a perfluoroelastomer providing the low refractive index medium. This combination yields a dielectric contrast large enough ($\Delta n \sim 0.22$) to form photonic structures with clearly discernible PBGs using as few as eight periods.

2.2. Materials and Methods

2.2.1. Samples Fabrication

Elastic Support: The DBRs were prepared on glass substrates ($25 \times 25 \times 1 \text{ mm}^3$) that had been pre-coated with a thick elastic layer serving as a mechanical support for the sample. This elastic layer was obtained by drop-casting 500 μL of a toluene solution (30 mg mL^{-1}) of a thermoplastic elastomer. Three types of polymers were evaluated as supports: Chemiton, Franprene (Franplast S.p.A.), and styrene–ethylene–butylene–styrene copolymer (SEBS, 66070-58-4, Sigma-Aldrich).

DBRs: The DBRs were fabricated through a layer-by-layer spin-casting process using polymer solutions. Tecnoflon PFR94 (SoYENSQO) served as the low refractive index component ($n_{\text{PFR}} \approx 1.32$) and styrene–butadiene–styrene copolymer (SBS) acted as the high refractive index material ($n_{\text{SBS}} \approx 1.5$). Further details are provided in the Results and Discussion section. Specifically, PFR94 was dissolved in Galden HT 110 (30 mg mL^{-1} , Solvay Specialty Polymers S.p.A.) whereas SBS was dissolved in toluene (30 mg mL^{-1}). Volumes of 200–300 μL of the polymer’s solution were alternatively deposited on top of each other to obtain the final multilayer via static spin coating. Prior to casting each SBS layer, the DBRs underwent a low-pressure cold-plasma treatment (Colibrì-1B-MF, Gambetti Kenologia) to enhance the surface tension of the underlying

PFR layer, as previously described.^[30] Tecnoflon PFR94 was employed without any cross-linking. Each device consisted of 8 bilayers (BLs).

2.2.2. Characterization

Before the mechanical characterization, each DBR with its elastomeric support was carefully detached from the glass substrate. Normal incidence reflectance and transmittance spectra were acquired using a custom-built optical fibers-based setup. For the reflectance measurements, illumination from a deuterium-tungsten halogen light source (Ocean Optics, spectral range of 230–2500 nm) was directed onto the DBR through a UV–vis–NIR optical fiber probe (Avantes FCR-7UVIR200-2-ME). The reflected signal was then collected and sent to a UV–vis detector (AvaSpec-ULS2048CL-EVO) and to a NIR detector (Arcoptix NIR Rocket, spectral range 900–2600 nm, resolution 8 cm⁻¹). To enable simultaneous evaluation of the mechanochromic effect, the reflectance setup was integrated with a custom designed strain device, as shown in the Appendix dedicated to the Supplementary Figures for Materials and Methods, Figure A1.1. The measured spectra were also analyzed using the transfer matrix formalism, following the methodology described in previous studies^[31] and in Chapter 1, employing as inputs the refractive index dispersion and the experimentally determined thicknesses of the polymer layers.

To investigate whether the photonic band structure is influenced by elongation, angle-resolved transmission spectra were collected at incidence angles ranging from 0° to 50° under three different strain conditions (0%, 50%, and 100%), using both parallel (P) and perpendicular (S) light polarizations. These measurements were performed by coupling a tensile testing device with a home-built transmission setup featuring an angular resolution of 2°.

Optomechanical characterization was carried out by integrating the optical fiber-based measurement system into a tensile testing machine (Instron 5565), as illustrated in Figure A1.2 of the Appendix of Supplementary Figures for Materials and Methods. Light from the Ocean Optics DH-2000-BAL source was delivered to the sample via optical fiber, and the transmitted signal was collected and directed to the UV–vis spectrometer previously described. Concurrently, the tensile machine recorded stress–strain curves of the samples. The same tensile device was also used for the mechanical testing of the drop-cast supports and the SBS material.

The effectiveness of the plasma treatment in activating the PFR surface was verified by measuring the contact angle of a 30 mg mL⁻¹ SBS solution in toluene, using the sessile drop method on a Theta Lite optical tensiometer (Biolin Scientific) before and after plasma exposure.

Atomic force microscopy (AFM) images of the supports were obtained using a Nanosurf NanoCore AFM operating in tapping mode. Photographs of the DBRs were captured with a smartphone.

2.3. Result and Discussion

Before proceeding with DBR fabrication, the optical characteristics of both PFR94 and the SBS copolymer were analyzed. Figure 2.1 presents their complex refractive index ($\tilde{n}=n+ik$). PFR94 exhibits a very low refractive index, approaching $n = 1.32$ at $\lambda = 1 \mu\text{m}$ (Figure 2.1a, black line) with minimal dispersion. As expected for a perfluorinated polymer, its extinction coefficient (Figure 2.1b, black curve) is nearly zero, showing only a slight increase up to $k=0.03$ at energies above 4 eV (wavelengths below 310 nm). This weak absorption is assigned to chemical groups incorporated into the polymer backbone to enable cross-linking, most likely bisphenol moieties.^[32, 33] The chemical structure shown in the inset of Figure 2.1b highlights the cross-linking sites with the symbol X. For the SBS copolymer, the refractive index rises from 1.53 at 0.5 eV (≈ 2500 nm) to 1.75 at 5 eV (≈ 250 nm), as illustrated in Figure 2.1a, red curve. Consistently, the extinction coefficient remains zero throughout the visible range, with the absorption onset appearing above 4 eV.

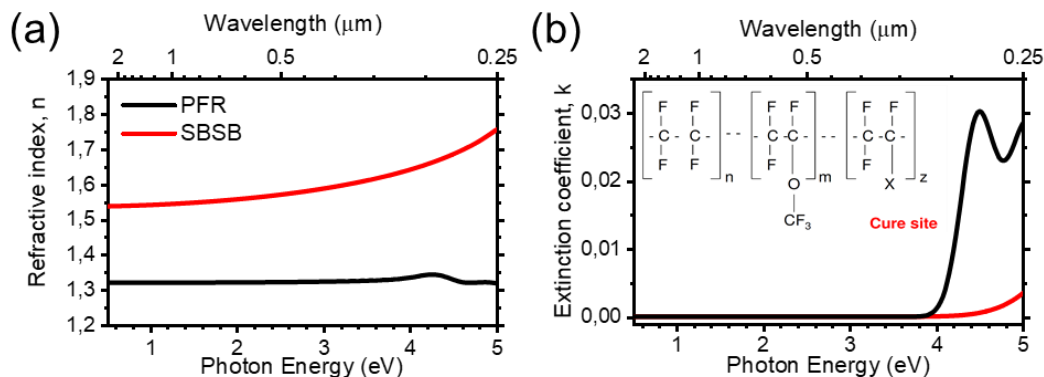


Figure 2.1: Refractive index (a) and extinction coefficient (b) of PFR94 (black curve) and SBS (red curve) plotted as functions of photon energy (bottom axis) and corresponding wavelength (top axis). The inset shows the chemical structure of PFR94, with the curing site indicated by the symbol X.

The optical constants of SBS closely match those of pure polystyrene, one of its constituent blocks, although slightly reduced values are observed, due to the presence of butadiene segments. [34]

The refractive index contrast between the two materials, a key parameter for determining the performance of PhCs, reaches approximately $\Delta n \approx 0.22$ in the near-infrared and increases toward shorter wavelengths, benefiting from the dispersion behavior of SBS.

In addition, to confirm the dielectric contrast between the two polymers, we also examined the feasibility of depositing thin SBS films onto the perfluorinated PFR94 layer. Perfluorinated materials are well known for their chemical inertness and low wettability, which makes the adhesion of a thin film to their surface a challenging task. Previous studies have shown that plasma treatment can enhance the wettability of perfluoropolymers. [30, 31] Therefore, we measured the contact angle of an SBS solution on a PFR94 film prepared as described in the Materials and Methods section, both before and after plasma treatment. This process is expected to promote adhesion and thus reduce the contact angle of the SBS solution. As shown in Figure 2.2a, before treatment the contact angle is about $60 \pm 1^\circ$, whereas after plasma exposure it decreases to $53 \pm 1^\circ$. Figure 2.2b shows a digital image of a droplet of SBS in toluene placed on the surface of an activated PFR94 film. These results confirm that, for DBR fabrication, surface activation is essential when working with fluorinated polymers.

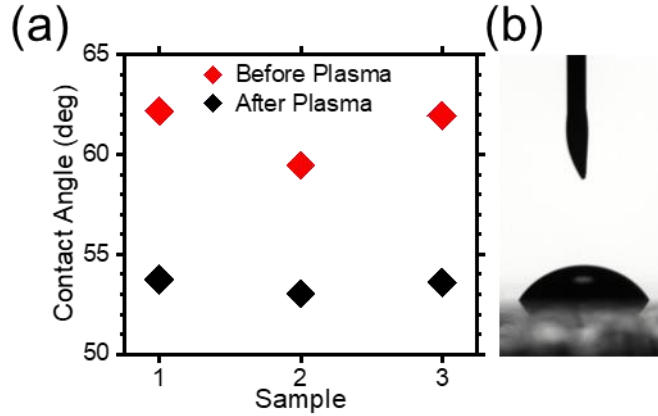


Figure 2.2: (a) Contact angle measurements for an SBS solution (30 mg/mL in toluene) on PFR94 thin films, comparing plasma-treated samples (black dots) with untreated ones (red dots); data represent three independent samples. (b) Digital photograph showing a droplet of SBS in toluene resting on the surface of a plasma-activated PFR94 film.

After verifying both the dielectric contrast between the two polymers and the wettability of PFR94 with SBS solutions, PFR94:SBS DBRs were fabricated as outlined in the Materials and Methods Section, using three different elastomeric supports made from commercial thermoplastic elastomers: Chemiton, Franprene, and SEBS copolymer. These samples are hereafter referred to as s-chemiton, s-franprene, and s-SEBS, respectively. Before evaluating the stress vs strain behavior of the elastomeric systems, a comprehensive optical characterization was carried out to confirm their optical performance and structural quality. Figure 2.3. presents the reflectance spectra along with digital photographs of the three samples.

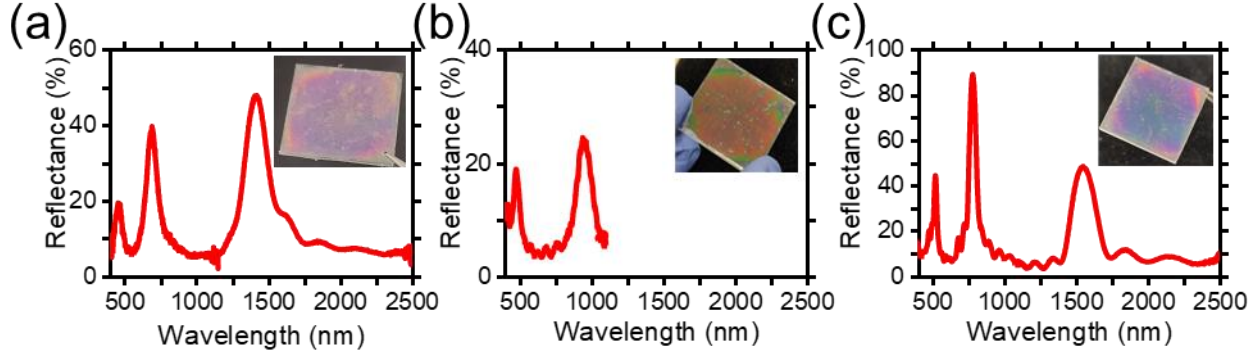


Figure 2.3: Reflectance spectra for s-chemiton (a), s-franprene (b), and s-SEBS (c). The insets display digital photographs of each sample prior to their removal from the glass substrate on which they were fabricated.

Figure 2.3a presents the spectrum obtained for s-chemiton, which features three reflectance peaks corresponding to photonic band gaps (PBGs) located at 1427 nm (0.876 eV), 691 nm (1.795 eV), and 456 nm (2.722 eV). These peaks appear broadened, likely due to minor variations in layer thickness or small structural defects. This interpretation is supported by the absence of background interference fringes, a feature typically observed in DBRs of exceptional optical quality as already reported in Chapter 1.

$$m\lambda_{\text{PBG}} = 2D \sqrt{n_{\text{eff}}^2 - \sin^2 \theta} = 2D n_{\text{eff}} \sqrt{\frac{d_L n_L^2}{D} + \frac{d_H n_H^2}{D}} \quad \text{Eq.2.1}$$

The spectral positions of the observed PBGs can be estimated using the Bragg–Snell law for unpolarized light at normal incidence on the DBR (Eq. 2.1). As already highlighted in Chapter 1, m denotes the diffraction order, D is the DBR periodicity ($d_L + d_H$), and d_L and d_H are the thicknesses of the low- (n_L) and high-index (n_H) layers, respectively. The effective refractive index (n_{eff}) is derived from the effective medium theory^[35] as the volume-weighted average of the refractive indices of PFR94 and SBS. According to this relation, PBGs are expected at integer fractions of the fundamental band gap (the one at the longest wavelength), assuming negligible refractive index dispersion. Indeed, the measured positions of the three diffraction orders scale well with the corresponding values of m . The digital image shown in the inset of Figure 2.3a reveals moderate color variations across the surface, suggesting a certain level of inhomogeneity within the sample.

For s-franprene (Figure 2.3b), two reflectance peaks are observed at 942 nm and 468 nm (1.316 and 2.649 eV), corresponding to the principal and higher-order PBGs, in agreement with the Bragg–Snell law. Also in this case, minor surface inhomogeneities are visible in the photograph (Figure 2.3, inset).

The s-SEBS DBR (Figure 2.3c) displays three PBGs centered at 1547 nm, 782 nm, and 524 nm (0.802, 1.586, and 2.366 eV). In this case, interference fringes are visible in the spectral background between the peaks, suggesting a higher degree of structural uniformity compared to the previous samples. Interestingly, unlike the other two systems, the second-order PBG here is more intense than the first. This is a known effect, typically arising from slight deviations in the optical thickness of the layers combined with minor scattering phenomena, which tend to impact the peak intensity more strongly as the wavelength shifts toward the shorter end of the spectrum.

The samples presented in Figure 2.3. were produced under identical fabrication conditions on three different supporting substrates. It is therefore relevant to examine the factors responsible for the variations observed in their optical behavior, since the choice of support appears to play a decisive role. Substrate roughness and adhesion properties are well known to influence DBR growth.^[30, 31] Consequently, we evaluated the wettability of the three supports and analyzed their surface morphology. The adhesion of the PFR94 solution in GALDEN HT110 was found to be optimal for all substrates tested. Figure 2.4a–c shows images of a droplet of solution on each surface, revealing a contact angle so small that it falls below the detection limit of our system. In contrast, the AFM micrographs in figure 4 indicate that Chemiton and SEBS exhibit relatively smooth morphologies, with only sporadic and uniformly distributed surface irregularities (panels d and f, respectively), whereas Franprene displays a considerably rougher surface texture (panel e). This difference is even more evident in the cross-sectional profiles shown in Figure 2.4g–i, where the Franprene sample presents larger vertical deviations (z-axis) compared to the other two materials. The root-mean-square roughness values extracted from the AFM images are approximately 1.2 nm for Franprene, 0.8 nm for Chemiton, and 0.4 nm for SEBS. These results confirm that the substrates display good wettability with PFR94 solutions. Nevertheless, subtle local variations in surface roughness and film homogeneity could influence this property at a microscopic scale, potentially impacting the uniformity of the first deposited layer and the subsequent stack formation.^[36]

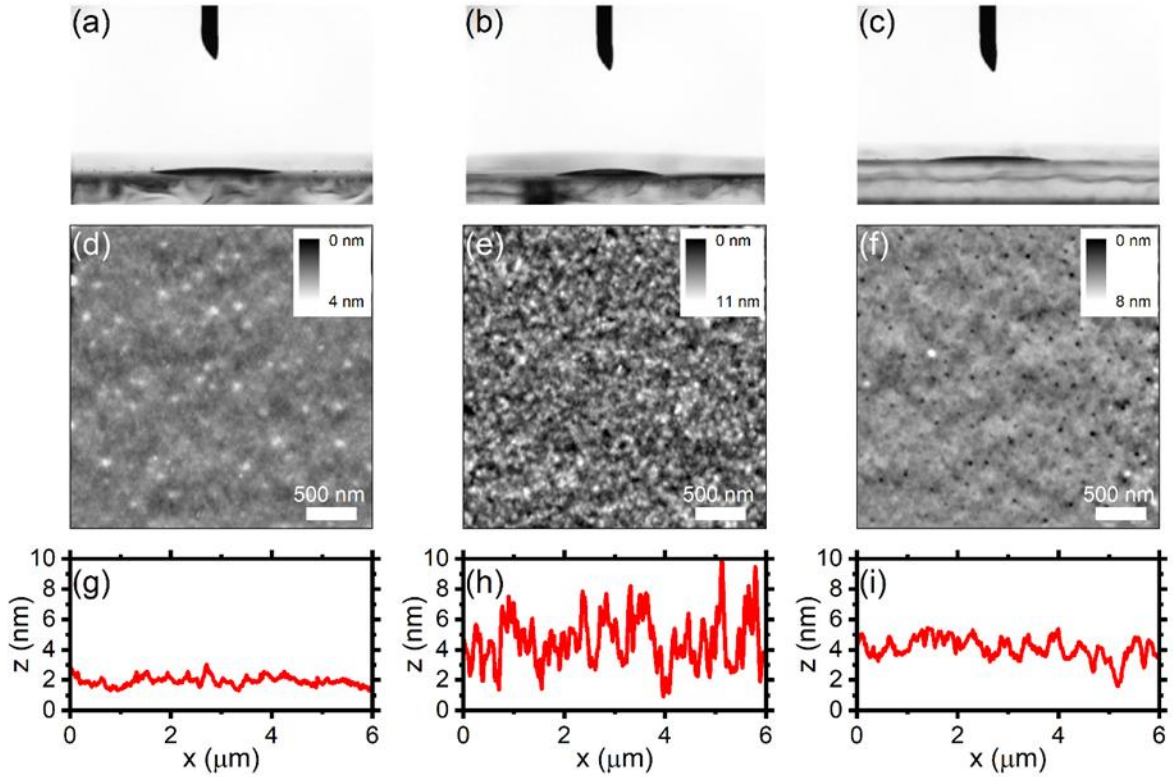


Figure 2.4: (a–c) Photographs showing the wetting behavior of the PFR94 solution (30 mg/mL in Galden HT110) on the surfaces of (a) Chemiton, (b) Franprene, and (c) SEBS. (d–f) AFM images and (g–i) corresponding cross-sectional profiles for (d,g) Chemiton, (e,h) Franprene, and (f,i) SEBS supports.

To verify that the spectral signature of the DBRs is influenced by the photon wavevector, as predicted by the band structure of planar PhCs, ^[14, 31] transmittance spectra of the samples were recorded as a function of the incident light angle for both p- and s-polarizations in the case of s-chemiton (Figure 2.5a). In these measurements, the PBG undergoes a hypsochromic shift as the incidence angle increases for both polarizations. Furthermore, in agreement with theoretical predictions, for p-polarization the PBG bandwidth narrows as the angle approaches the Brewster angle, whereas for s-polarization the bandwidth is maintained or even increases. ^[14, 23] The observed broadening of the PBG for s-polarization is attributed to the previously discussed inhomogeneous broadening, which makes the DBR's optical response particularly sensitive to defects. This effect becomes more pronounced at larger incidence angles, where a wider portion of the sample is probed. The data are presented as contour plots, with the y-axis representing the

incidence angle, the x-axis representing the wavelength, and the transmittance indicated by the color scale. The PBGs are represented by the oranges bands on blueish background.

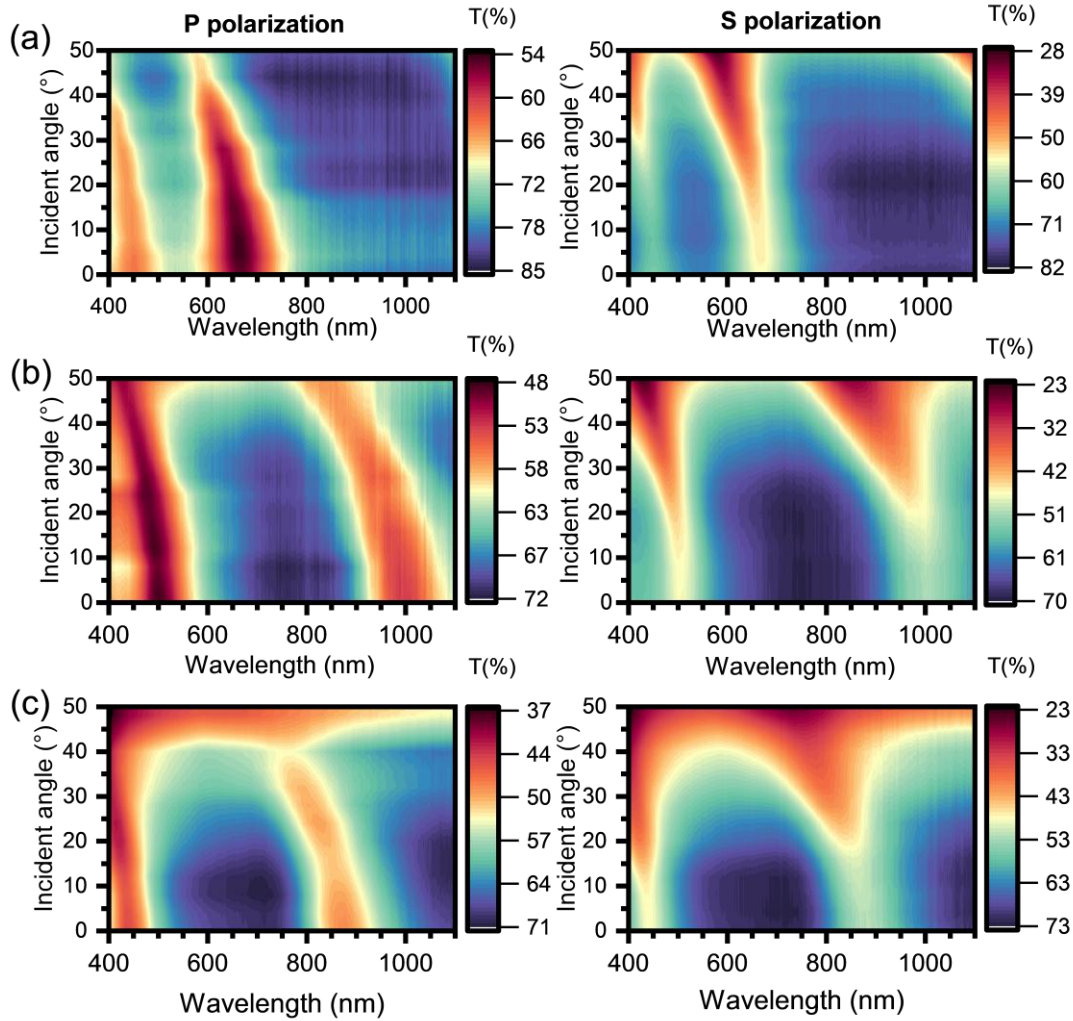


Figure 2.5: Transmittance spectra were acquired for incidence angles ranging from 0° to 50° in 4° increments, at three different strain levels: (a) 0%, (b) 50%, and (c) 100%. Measurements were performed for parallel (P-polarization, left column) and perpendicular (S-polarization, right column) light polarizations in the case of s-chemiton.

2.3.1. Mechanochromic Response

The pronounced mechanochromic behavior of the DBRs under mechanical strain is clearly visible to the naked eye, as the sample color gradually shifts from reddish-purple to cyan-green and eventually to blue (Figure 2.6).

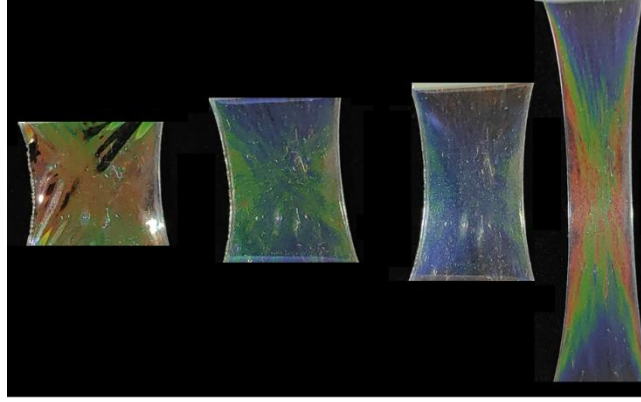


Figure 2.6: Digital image of the chromatic change occurring for s-chemiton.

To gain a more detailed understanding of this effect, we recorded the optical spectra of the samples as a function of applied strain using two custom-built experimental setups. The first setup allowed the measurement of reflectance variations with strain, while the second was designed to acquire transmittance spectra during standard stress–strain tests. For these measurements, all DBRs were detached from their original glass substrates. Figure 2.7 show the stacked reflectance spectra at various strain levels ($\epsilon = (l - l_0) / l_0 \times 100$), recorded both during stretching (l) and after returning to the initial length (l_0), for the three DBRs. Spectra were collected in the 300–1100 nm range. The elongation range extended from $\epsilon = 0\%$ up to $\epsilon = 400\%$ for s-chemiton and s-franprene, while for s-SEBS it was limited to $\epsilon = 250\%$ due to experimental reasons. In the latter case, removal from the glass substrate likely induced defects or folding, restricting further stretching. Generally, detaching the samples from the substrate caused a premature blue shift of the PBG due to permanent structural deformation. Reversibility and possible plastic deformation were then assessed by bringing the samples back to $\epsilon = 0\%$ after stretching, focusing on the second-order PBG features that remained detectable throughout the entire mechanical deformation cycle.

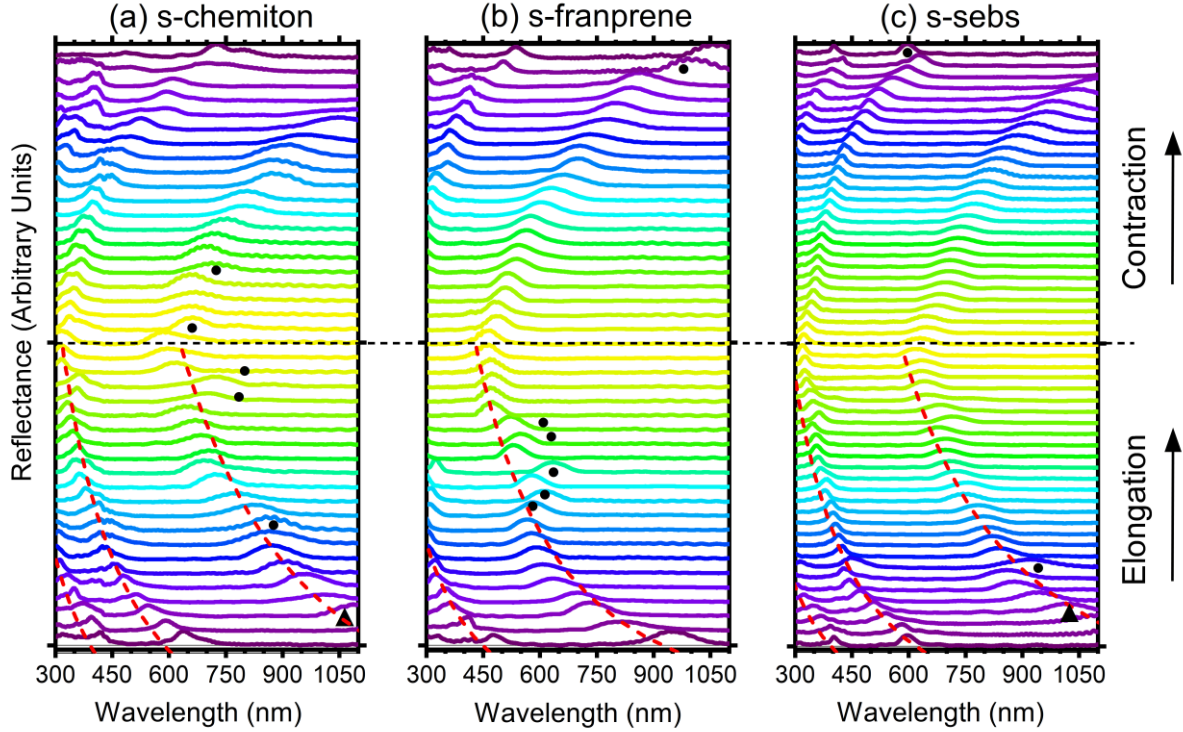


Figure 2.7: Stacked reflectance spectra for (a) s-chemiton, (b) s-franprene, and (c) s-SEBS at different strain (ϵ) levels ranging from 0% to 400% (up to 250% for s-SEBS) in 20% increments. The lower section of each plot corresponds to the elongation phase, while the upper section represents the contraction phase. The horizontal dashed line marks the maximum elongation point and the onset of contraction. The symbol “▲” identifies the strain value at which the first PBG becomes visible within the investigated spectral range; “●” denotes an anomalous spectral

For s-chemiton (Figure 2.7a), all three PBGs exhibit a shift toward shorter wavelengths as strain is applied, followed by a reverse shift when the strain is released. The first-order PBG becomes detectable at 1087 nm only when ϵ reaches 40% (indicated by the triangle “▲”) and continuously shifts to 578 nm at $\epsilon = 400\%$ (marked with the dashed line). The second-order PBG, initially at 637 nm, shifts down to 318 nm and then recovers to 720 nm after relaxation. Similarly, the third peak moves from 421 nm into the UV region (beyond detection) for $\epsilon > 40\%$, and returns to 484 nm upon release. Overall, the spectra display a predominantly elastic response with slight plastic deformation. The wavelength shifts are not perfectly monotonic, with a few anomalies present (dots “●” in Figure 2.7a), likely due to local sample damage or slippage in the clamping system.

The s-franprene DBR (Figure 2.7b) follows a similar trend up to $\epsilon = 400\%$. The first-order PBG, starting at 946 nm in the unstrained state, shifts to 451 nm at maximum extension, then recovers

to 1000 nm after release. The higher-order PBG observed at 479 nm in the relaxed state moves into the undetected UV range during stretching, then returns to 497 nm upon recovery. As in the previous case, the reversibility is fairly good, although some strain values show anomalous peak positions (dots “●” in Figure 2.7b).

For s-SEBS (Figure 2.7c), stretching was limited to $\varepsilon = 250\%$. The first-order PBG (originally at 1550 nm, see Figure 2.7c in the previous section) appears within the investigated spectral range only at $\varepsilon = 40\%$ (triangle “▲” in Figure 2.7c) and shifts to 647 nm at maximum strain. The second-order peak moves from 598 to 322 nm before returning to 595 nm, while the third shifts from 400 nm into the UV and back to 395 nm. This DBR exhibits fewer anomalous wavelength positions (dots “●” in Figure 2.7c) compared with the other samples, likely due to the smaller maximum strain applied.

Further confirmation of the optical integrity of the elastomeric DBRs under strain comes from the transmittance spectra of s-chemiton samples stretched to $\varepsilon = 50\%$ (Figure 2.5b) and $\varepsilon = 100\%$ (Figure 2.5c). The same features described for the unstrained case (Figure 2.5a) are present, apart from the expected blue-shift of the PBGs. These results indicate that the photonic band structure remains intact under deformation.

As predicted by Eq 1, the hypsochromic shift of all PBGs under strain results from the decrease in the bilayer thickness (the structural periodicity) of the nanostructure. Previous studies have shown that the PBG position in strained samples, $(\lambda_{\varepsilon,m}(\varepsilon))$, depends on both the applied strain and the initial PBG wavelength $(\lambda_{0,m})$, such that:

$$\lambda_{\varepsilon,m}(\varepsilon) = \frac{\lambda_{0,m}}{\sqrt{1 + \varepsilon}} \underset{\varepsilon \rightarrow 0}{\sim} \lambda_{0,m} \left(1 - \frac{1}{2} \varepsilon \right) \quad \text{Eq. 2.2a}$$

$$\Delta\lambda_{\varepsilon,m} = \lambda_{\varepsilon,m}(\varepsilon) - \lambda_{0,m} = \underset{\varepsilon \rightarrow 0}{\sim} -\frac{\lambda_{0,m}}{2} \varepsilon \quad \text{Eq. 2.2b}$$

These relationships were verified by comparing the experimentally measured shift of the m^{th} PBG with the theoretical $\Delta\lambda_{\varepsilon,m}$ values obtained from eq 2.2, using the measured $\lambda_{0,m}$ as input.

The calculated PBG positions were then overlaid onto the stack plots shown in Figure 2.7 and are represented by the red dashed line. The close agreement between theoretical predictions and

experimental measurements enables the extrapolation of $\lambda_{\epsilon,m}$ values beyond the explored spectral range, as well as the estimation of the expected mechanochromic sensitivity (Table 1).

For this purpose, we focus on the linear region of the spectral shift curves, which occurs at low strain levels ($\epsilon < 20\%$). In this regime, the approximation $\lambda_{0,m}/2 = -\lambda_{0,1}/2m$ can be applied. Consequently, given a fixed instrumental spectral resolution (1.4 nm in our case), the mechanochromic sensitivity ($MS_{\epsilon}^{\lambda,m} = \Delta\lambda/\epsilon$, where $\epsilon = \frac{\Delta l}{l_0}$) is determined by both the diffraction order of the PBG and its corresponding wavelength (Equation 2.3):

$$MS_{\epsilon}^{\lambda,m} = -\frac{\lambda_{0,m}}{2} 10^{-2} \sim -\frac{\lambda_{0,1}}{2m} 10^{-2} \quad \text{Eq. 2.3}$$

Accordingly, $MS_{\epsilon}^{\lambda,m}$ increases as the PBG shifts toward longer wavelengths. Equation 3 is based on two assumptions: (i) the refractive index of the polymers is spectrally constant, and (ii) it remains unaffected by the applied strain within the linear regime ($\epsilon < 20\%$). The first assumption is valid for the polymers used in this study, although it becomes less accurate in the pre-resonant spectral range, where the refractive index displays marked optical dispersion (see, for instance, the visible range for polyvinyl carbazole and the Abbe number of other high-refractive-index polymers). The second assumption is also reasonable within the linear regime; however, for $\epsilon > 20\%$, stretching may induce significant anisotropy in the polymer's optical properties.

To evaluate this effect, we compared reflectance spectra collected during stretching with modelled data, using the refractive index of the unstretched samples (Figure 2.8) and treating the structural periodicity (D) as a fitting parameter under the assumption $\Delta d_L = \Delta d_H$. The modelling employed the transfer matrix method, a well-established approach for simulating optical responses in multilayer systems such as DBRs, already introduced in Chapter 1. The strong agreement between experimental and simulated spectra in Figure 2.8, together with the angle-dependent transmittance spectra in Figure 2.5, confirms the spectral signature of the photonic nanostructure. It also demonstrates that the photonic structure is maintained even under substantial deformation, without delamination, and that any strain-induced anisotropy has a negligible effect within the studied spectral range.

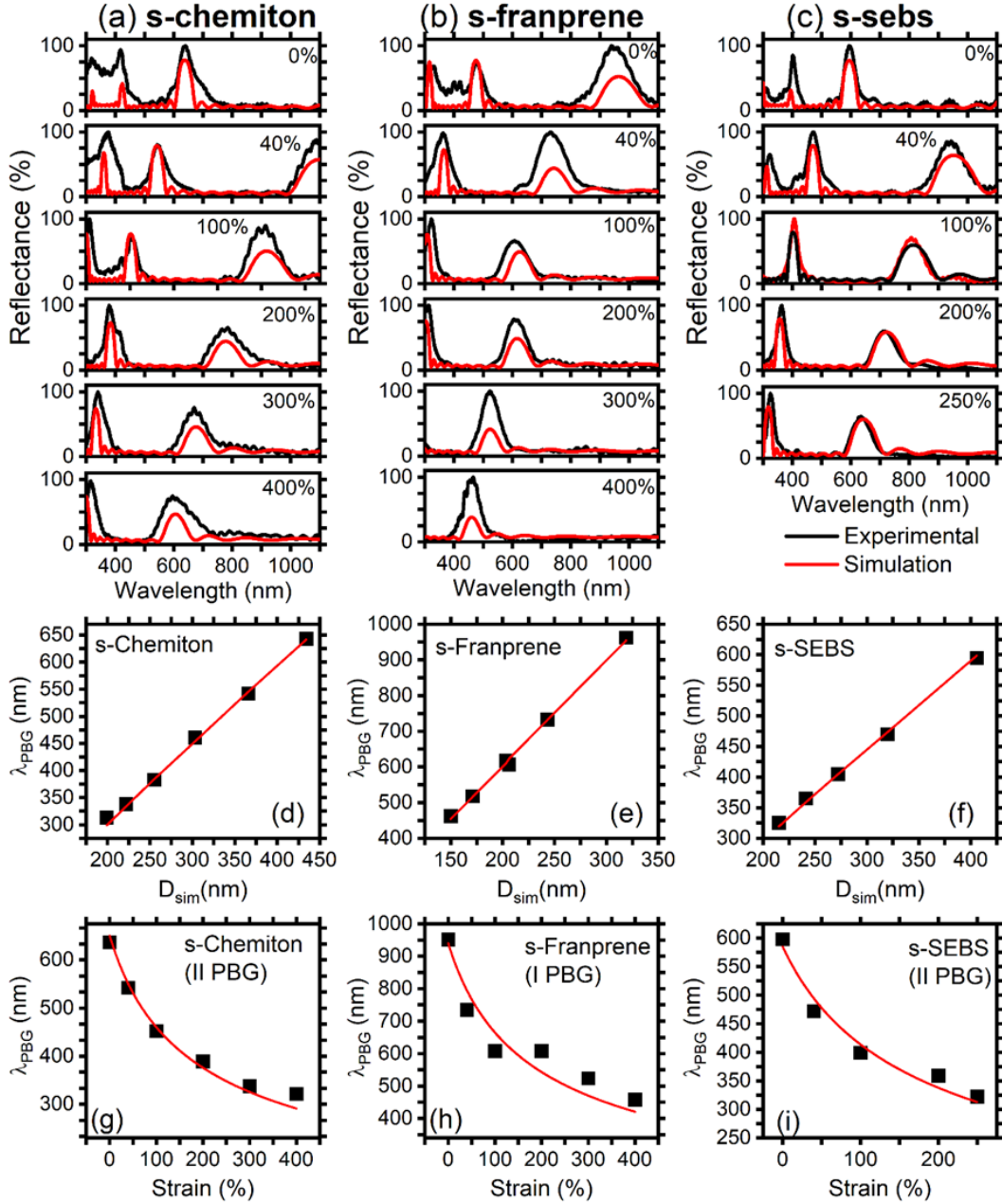


Figure 2.8: Experimental and simulated spectra at different elongations for (a) s-chemiton, (b) s-franprene, and (c) s-SEBS. Panels (d–f) show the second-order PBG spectral positions as a function of the simulated photonic structure periodicity (D_{sim}) for s-chemiton and s-SEBS, while panel (e) shows the first-order PBG spectral position versus D_{sim} for s-franprene. Black dots represent experimental data, and the red line corresponds to the simulations. Panels (g–i) report the PBG spectral positions at increasing strain: experimental data (black squares) and fits according to eq 2.2 (red line).

For s-franprene, the fit quality is lower, likely due to the greater number of anomalies in its mechanochromic response, which introduce local disorder not considered in the model that assumes an ideal periodic lattice with flat interfaces. Additional small mismatches between simulation and experiment are attributed to intrinsic fabrication imperfections. Importantly, spectral fitting is necessary to determine the thicknesses of the high- and low-refractive-index layers (d_H and d_L), since in the Bragg–Snell law (Equation 2.1) these parameters determine both D and n_{eff} . Equation 2.1 is therefore mainly useful for validating the model once these values are established.

Figure 2.8d,e,f compares experimental (black points) and calculated (red line) $\lambda_{\epsilon,2}$ as a function of the simulated periodicity (D_{sim}). The data show excellent agreement and reveal a linear relationship between $\lambda_{\epsilon,2}$ and D_{sim} , with a slope of 3/2, consistent with the Bragg–Snell relation. From eq 1, $\lambda_{\epsilon,m} = [2n_{\text{eff}}/m] D$, for $m=2$ and $n_{\text{eff}}=1.45$, the expected slope is approximately 3/2. Finally, Figure 2.8g,h,i presents the PBG spectral positions for the three samples derived from the spectra in panels a–c. In all cases, the PBG shifts toward shorter wavelengths as strain increases, exhibiting a nonlinear trend. This behavior follows Eq 2.2, as indicated by the strong correlation between experimental results and the fitted curves (red dashed lines in Figure 2.7).

Table 1 summarizes the experimental and calculated $MS_{\epsilon}^{\lambda,m}$ values for the sensors. Regarding the PBG wavelength at rest, discrepancies arise when comparing optical characterizations before and after sample removal from the fabrication substrate, as shown in Figure 2.3. In particular, a blue shift is observed, likely caused by the removal process, which, being challenging, can permanently modify the structure and alter its optical response. Overall, experimental data generally exhibit a larger response than predicted by calculations. This deviation is assigned to the assumptions of linear dependence between $\lambda_{\epsilon,m}$ and ϵ and a strain-independent refractive index.

Table 1. Wavelength of the PBG at rest for each order ($\lambda_{\text{PBG},m}$), spectral shift for $0\% < \varepsilon < 20\%$ ($\Delta\lambda_{\text{PBG}}$), theoretical (from Eq. 2) and experimental $\text{MS}_{\varepsilon}^{\lambda,m}$ for $\varepsilon < 20\%$, Optical Poisson ratio, and Young modulus of the substrates.

Diffracti on order, m	$\lambda_{\text{PBG},m}$ (nm)	$\Delta\lambda_{\text{PBG}}$ (nm) Theo (from Eq. 2)	$\Delta\lambda_{\text{PBG}}$ (nm) experimen tal	$(\text{MS}_{\varepsilon}^{\lambda,m})_{\text{theo}}$ (nm/%)	$(\text{MS}_{\varepsilon}^{\lambda,m})_{\text{exp}}$ (nm/%)	Optical Poisson ratio	Substrat e Young Modulus (MPa)
s-chemiton							
1	1270*	127	N.A.	-6.3*	N.A.	N.A.	3.5
2	636	64	46	-3.2	-2.3	0.36	
3	406	41	25	-2	-1.2	0.31	
s-franprene							
1	946	95	137	-4.7	-6.9	0.72	9.2
2	479	48	70	-2.4	-3.5	0.73	
3	330*	33	N.A.	-1.65	N.A.	N.A.	
s-SEBS							
1	1188*	119	N.A.	-5.9	N.A.	N.A.	6.2
2	594	59	56	-3.0	-2.8	0.47	
3	402	40	34	-2.0	-1.7	0.42	

*Estimated from Eq. 2.2.

From Figure 2.7, it is also possible to extract the Poisson ratio (ν in Equation 2.3) using a simple optical measurement. Here, we assume a constant effective refractive index for $\varepsilon < 20\%$ and identical thickness variations for the high- and low-refractive-index layers, such that $\Delta d_L = \Delta d_H = \frac{1}{2}\Delta D$. Defining $d\varepsilon_x, d\varepsilon_y$, and $d\varepsilon_z$ as the sample's dimensional changes along the elongation axis (x), the transverse axis (y), and the direction normal to the surface (z), the Poisson ratio is given by $\nu = d\varepsilon_z/d\varepsilon_x$ (eq 2.3).

Since the Poisson ratio is strictly defined for isotropic materials, we approximate $d\varepsilon_z = d\varepsilon_y$ for $\varepsilon < 20\%$. This approximation is supported by direct measurements of the sample width during elongation, yielding $d\varepsilon_y/d\varepsilon_x \approx 0.5$, consistent with the values reported in Table 1. Under these assumptions, and considering that the PBG position (λ_{ε}) is linearly proportional to D and n_{eff} (eq 2.1), one can write:

$$\nu = -\frac{d\varepsilon_z}{d\varepsilon_x} = \frac{d\varepsilon_y}{d\varepsilon_x} = \frac{D_{\varepsilon} - D}{D} \bigg/ \varepsilon_x \quad \text{Eq. 2.3a}$$

$$\frac{D_{\varepsilon} - D}{D} = \left[\frac{\lambda_{\varepsilon}}{2n_{\text{eff}}(\lambda_{\varepsilon})} - \frac{\lambda_{\varepsilon=0}}{2n_{\text{eff}}(\lambda_{\varepsilon=0})} \right] \frac{2n_{\text{eff}}(\lambda_{\varepsilon=0})}{\lambda_{\varepsilon=0}} \approx \frac{\lambda_{\varepsilon} - \lambda_{\varepsilon=0}}{\lambda_{\varepsilon=0}} \quad \text{Eq. 2.3b}$$

Equation 2.3b defines the optical strain. As shown in Figure 2.8 and according to Eq. 2.1, the thinning of the layers can be directly calculated from the PBG spectral shift measured when the sample is strained.

The optical Poisson ratios determined for the DBRs range between 0.3 and 0.7, values comparable to those reported for typical elastomers (~ 0.5).^[37,38] Interestingly, other polymer photonic crystals (PhCs) have been reported to exhibit much smaller ratios (0.22–0.29).^[39] Li et al. assigned this deviation to the intrinsic mechanical differences between the periodic, multicomponent nanostructure of a PhC and a homogeneous elastomer. Generally, a Poisson ratio approaching zero indicates structural collapse upon stretching, as observed in open-cell foams.^[40]

In our case, the optical Poisson ratios of DBRs grown on different substrates correlate with the Young's modulus of the supports, as derived from stress–strain measurements (Table 1 and Figure 2.9). This suggests that the substrate plays a dominant role in governing the DBRs' mechanical behavior, influencing both layer deposition and layer thinning during elongation. Indeed, Figure 2.9 shows a comparison between the stress-strain curves of the three elastomeric supports as a complete elongation and contraction cycle. From the complete stress vs strain curves, a rather elastic behavior of the support can be observed as compared to the non-elastic behavior of the DBR. Similar to the overall system, the curves of the monolayers do not completely overlap in the elongation and contraction phase, so that it is not possible to assess a complete recovery of the mechanical properties after deformation. However, stress-strain data for the bare substrates are not far from reversibility. Comparing the mechanical behavior of the monolayers of bare materials at low strains (0-10%), an increase in the modulus of elasticity can be observed as reported in Table 1 from chemiton, to franprene and then to SEBS. Unfortunately, mechanical properties of bare PFR films were investigated as it was not possible to realize good quality thin free-standing samples suitable for the measurement.

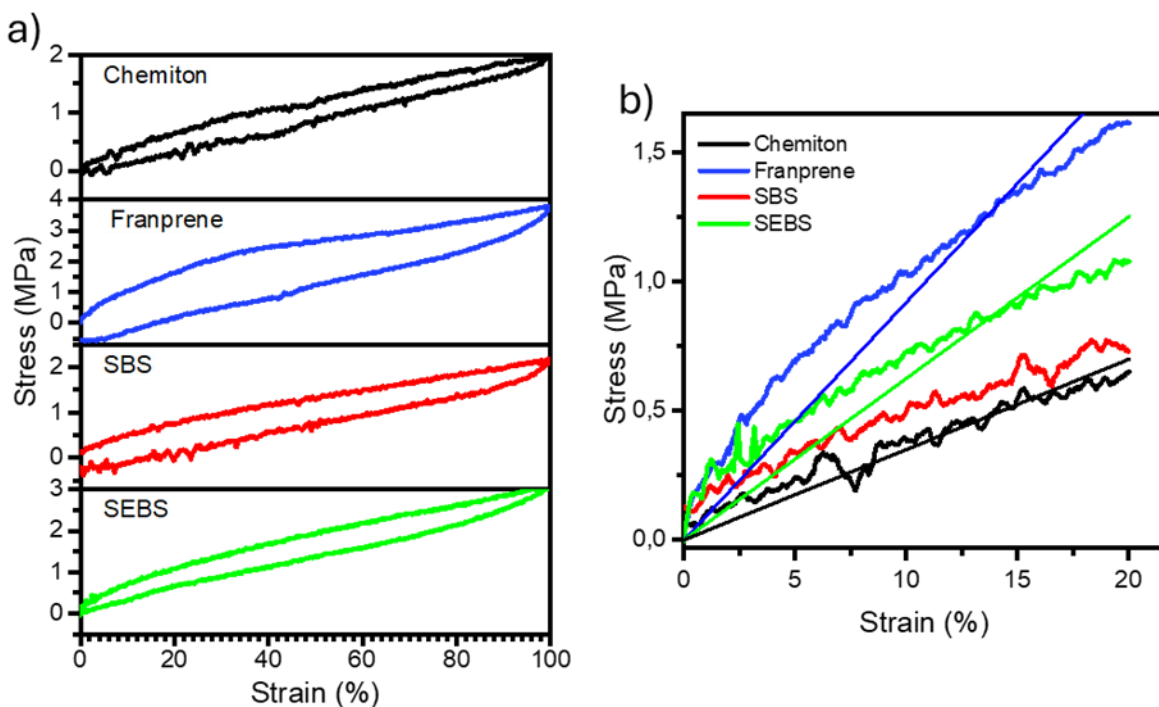


Figure 2.9: (a) Comparison between the stress vs strain curves of the three substrates and of the high index medium at 100% elongation and its recovery. (b) zoom of the data on 0-10% strain range with relative linear fit for the determination of the Young modulus for chemiton, franprene and SEBS. PFR94 was not mechanically investigated as it is not possible to realize a free-standing sample of suitable thickness and requested uniformity for the measurements.

To further probe these findings, we examined the optical stress-strain curves of DBRs to better understand their mechanical response. For this purpose, we coupled an optical setup to a tensiometer (see Materials and Method section) to simultaneously record sensor transmittance and stress-strain data. As a proof of principle, we focused on s-chemiton to quantify both spectral-strain and spectral-stress responses.

Figure 2.10a presents the reflectance spectra of s-chemiton as a 3D contour plot for strains ranging from 0 to 100%, applied at 3 mm/min, during both elongation and contraction. The mechanochromic effect is clearly observed across the entire spectral range during both stretching ($\epsilon = 0-100\%$) and release ($\epsilon = 100-0\%$). Despite the different setup, the sample exhibits behavior consistent with that reported in Figure 2.7. The sensor's color change along with strain is also visually evident in the photographs of Figure 2.10b, where the sample transitions from red to green and finally to blue during elongation is reported.

Figure 2.10c shows the stress–strain behavior of the DBR during elongation (black) and contraction (red) up to 100% strain. The high-strain endpoint was chosen arbitrarily and does not correspond to the breaking point, as no attempt to fracture the structure was made. The elongation–contraction curves exhibit hysteresis, indicating nonideal elastic behavior with a contribution from plastic deformation, much more relevant than for the bare materials (Figure 2.9). DBRs behavior is common for similar elongations.^[38] A reasonably linear stress–strain region is observed up to $\varepsilon \approx 10\%$, from which a Young’s modulus of 9 MPa was calculated. Beyond this region, nonlinear behavior with a yield point occurs at $\varepsilon \approx 18\%$. Simultaneously, the spectral response was recorded during elongation and contraction. Figure 2.10d and Figure 2.10e show the second-order PBG wavelength as a function of strain and stress, respectively, during elongation (black) and contraction (red), highlighting the mechanochromic effect discussed previously. Linear fitting up to $\varepsilon \approx 10\%$, yields a strain mechanochromic sensitivity of $MS_\varepsilon = \Delta\lambda_{\text{PBG}}/\Delta\varepsilon = -1.7 \pm 0.2 \text{ nm}/\%$ and a stress mechanochromic sensitivity of $MS_\sigma = \Delta\lambda_{\text{PBG}}/\Delta\sigma = -78 \pm 7 \text{ nm}/\text{MPa}$ for the second-order PBG. Fitting the relaxation data provides $MS_\varepsilon = \Delta\lambda_{\text{PBG}}/\Delta\varepsilon = 2.5 \pm 0.1 \text{ nm}/\text{strain } (\%)$ and $MS_\sigma = \Delta\lambda_{\text{PBG}}/\Delta\sigma = -72 \pm 3 \text{ nm}/\text{MPa}$, confirming the system’s nonideal elasticity. Comparison with literature data shows that our results are consistent with other photonic structures, although few DBRs have been reported and typically involve block copolymers; to our knowledge, no MS_σ values for elongation have been previously reported. These sensitivities demonstrate that even small deformations can be reliably detected with modest spectral resolution or by the naked eye. The response is also fast, with chromatic changes occurring within the spectrometer response time ($<100 \text{ ms}$). To evaluate reversibility, 10 elongation–contraction cycles (0–100% at 3 mm/s) were performed on the same sample. Figure 2.10f and Figure 2.10g show stress and PBG wavelength shifts for each cycle. Black dashed lines mark 0% elongation, red dashed lines 100%. The data demonstrate consistent and reversible performances, confirming the suitability of these DBRs for optomechanical sensing. This also indicates the optical response remains intact throughout the measurements, ruling out delamination or collapse of the nanostructure, i.e. any issue related to interlayer adhesion. In summary, mechanochromic sensitivity depends not only on the mechanical properties of the materials but also on the PBG spectral position and diffraction order. This effect – never investigated before – might allow a fine tuning of our sensors to different mechanical conditions.

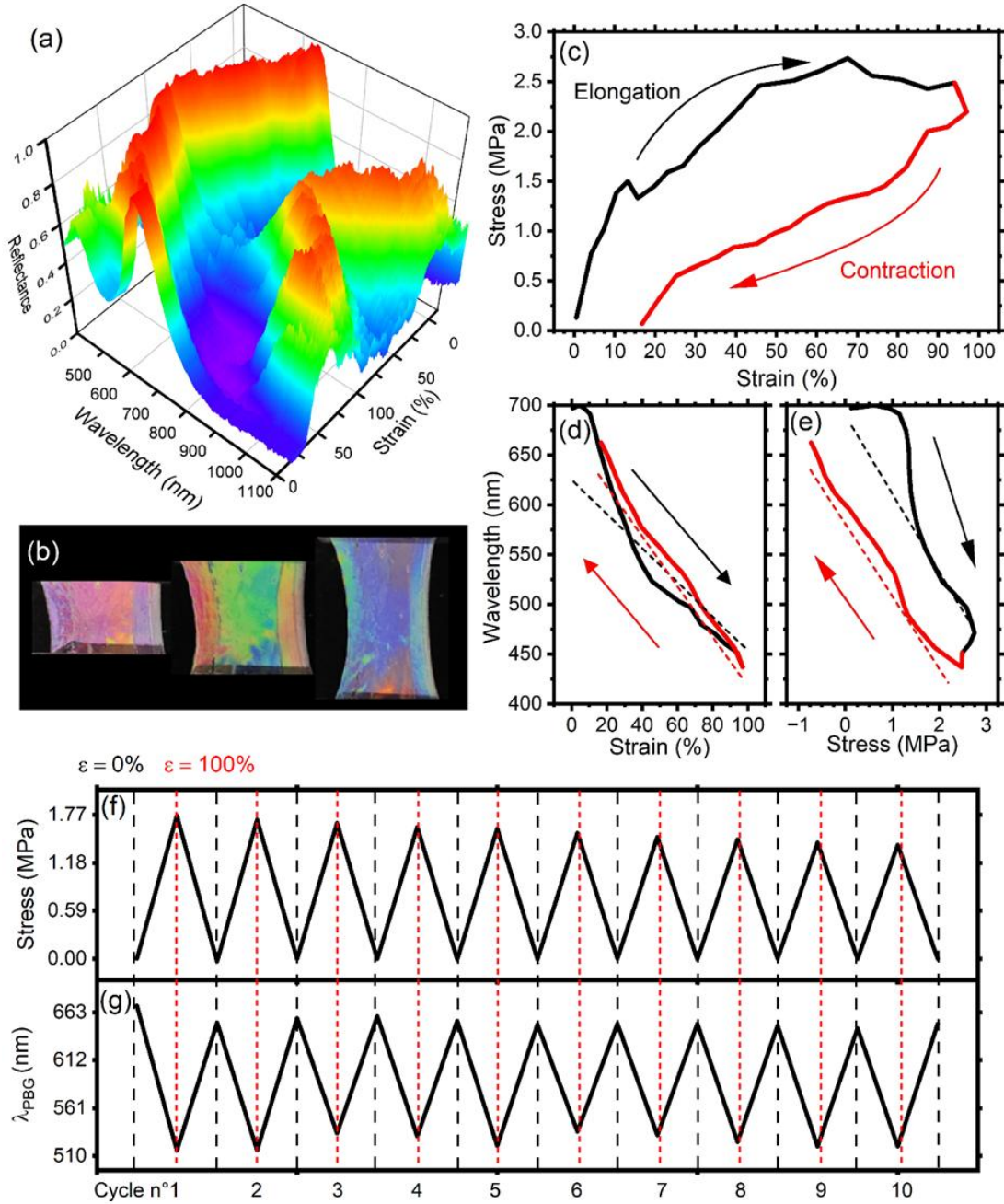


Figure 2.10: Optomechanical characterization of s-chemiton: (a) 3D contour plot of reflectance spectra as a function of strain (up to 100%) during elongation and contraction (100–0%); (b) image of the sample showing the color shift from red to green to blue upon stretching; (c) stress–strain curve for elongation (black) and contraction (red); spectral position of the second-order PBG as a function of strain (d) or stress (e) (black: elongation; red: contraction); (f, g) stress and PBG wavelength vs strain at fixed values of 0% (black dashed lines) and 100% (red dashed lines) for 10 elongation–contraction cycles.

2.3.2. Second-generation Stretchable DBRs

Driven by scientific curiosity and motivated by the promising, yet imperfect results so far obtained with the first-generation sensors, we sought to address the remaining challenges and further refine the fabrication process. While the initial samples successfully demonstrated mechanochromic behavior, minor inhomogeneities and variations in layer thickness limited the precision and reproducibility of strain-dependent optical measurements, motivating efforts to improve the correlation between optical response and mechanical stress, thereby bringing us closer to the ultimate goal of a fully functional sensor. Guided by these observations, we aimed to develop a fabrication strategy capable of producing structures that did not necessarily require a supporting substrate, thereby enhancing both mechanical robustness and versatility. In particular, our objectives included increasing the number of deposited layers without compromising structural quality, as well as laying the groundwork for the realization of stretchable microcavities, which will be discussed in a subsequent chapter. To achieve these goals, a dynamic spin coating method was implemented as an alternative to the previously employed static approach, as described in the Materials and Methods section. In addition, SEBS grafted with maleic anhydride (SEBS-g-MAH) was employed as an alternative high-refractive-index component to SBS, as it is expected to provide improved interfacial adhesion, the molecular structure of the SEBS-MAH copolymer is shown in Figure 2.11

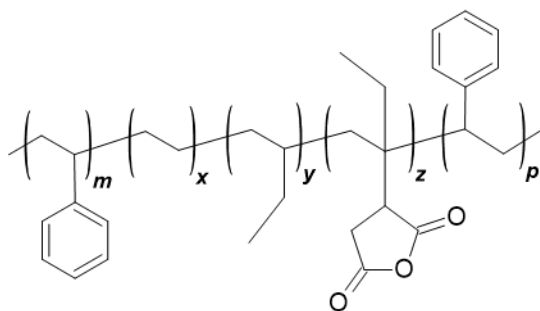


Figure 2.11: Molecular Structure of SEBS-MAH

This technique offered improved control over layer deposition, enabling a more precise and easier tuning of individual layer thicknesses. Furthermore, this approach reduced polymer and solvent consumption, shortened fabrication times, and offered greater flexibility for process optimization, allowing the production of samples with an increased number of layers without sacrificing optical performance, and even improving overall structural and optical quality. Preliminary observations

indicate that samples produced using this method exhibit enhanced optical properties, including sharper photonic band gaps and more pronounced interference features, reflecting a notable improvement in structural quality. In Figure 2.12 we report a comparison between the mechano-optical responses of two samples with the same number of layers and the same constituent materials, one fabricated via static spin coating (left panel) and the other via dynamic spin coating (right panel). In the insets, photographs of the corresponding samples are shown. The static spin-coated sample exhibits a less vibrant coloration and presents more surface defects, including halos and non-uniformities characteristic of the static deposition process. In contrast, the dynamically spin-coated sample displays a brighter and more uniform color, with surface imperfections attributable mainly to manual handling rather than to the coating method itself. The data are presented as color maps, where the y-axis reports the applied strain during elongation (lower region) and contraction (upper region), the x-axis represents the wavelength, and the color scale corresponds to the transmittance percentage. In both samples, the photonic bandgap (PBG) appears as a reddish band against a bluish background. In the static spin-coated sample, however, the PBG is considerably broader and exhibits several defects that locally make it difficult to distinguish from the background. This poor definition complicates the correlation between the optical response and the strain experienced by the structure, which is precisely the function that our sensor must reliably perform. Moreover, in this sample it is not possible to observe characteristic features such as interference fringes, likely due to the irregularities introduced by the static coating process. In contrast, the dynamically spin-coated sample shows a much more clearly defined PBG, which stands out distinctly from the background. The narrower PBG makes it easier to track its spectral position as a function of strain. Furthermore, well-defined interference fringes are clearly visible across the entire spectrum and can even be seen shifting with the PBG during deformation. This behavior provides additional evidence of the superior optical quality and structural uniformity of the dynamically deposited sample. In the final part of the contraction cycle, at nearly 20% strain, a slack in the sample can also be observed: the PBG shifts back toward shorter wavelengths, likely due to the formation of a small gap or defect in the film and to a resulting change in the way the deformation is applied.

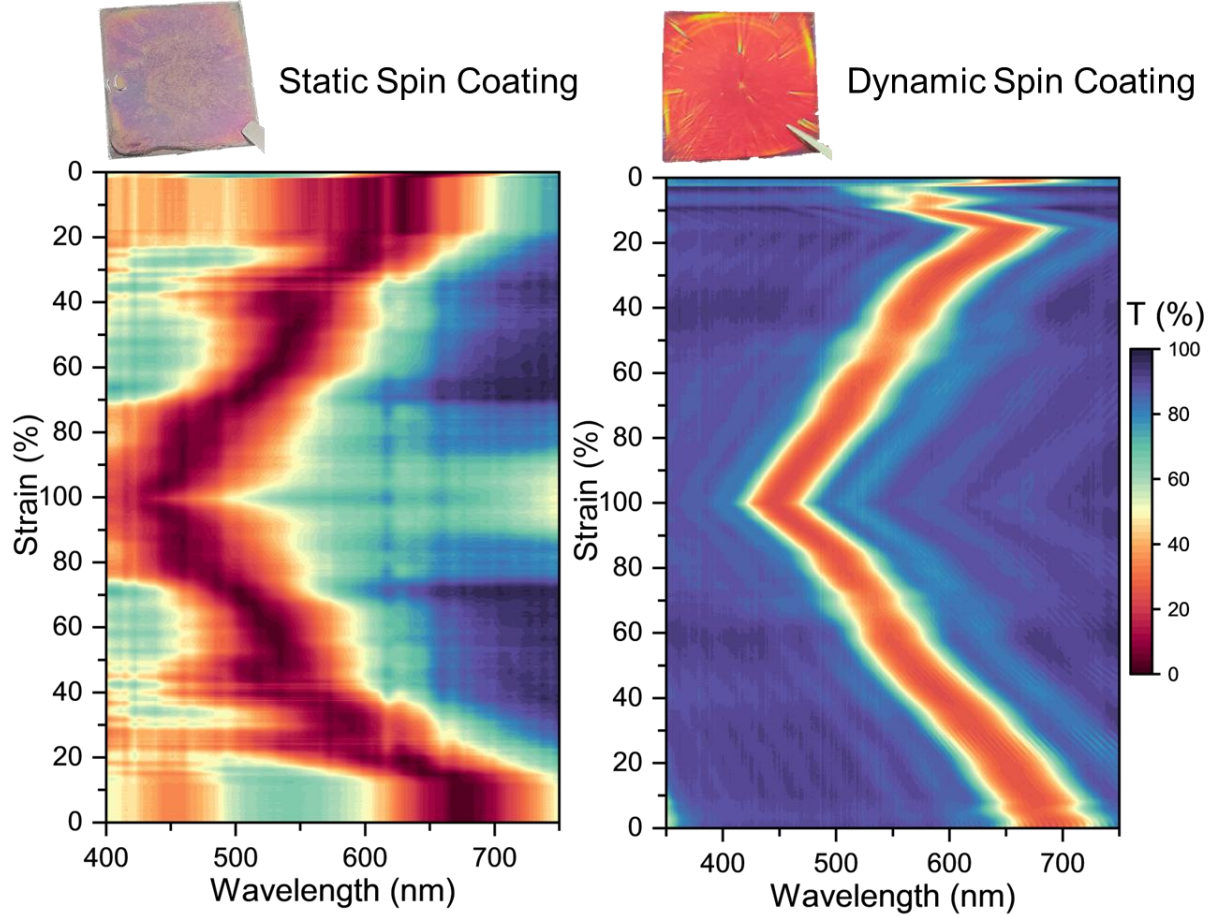


Figure 2.12: Digital images and of color maps with the strain (0-100 %) on the y axis, the wavelength on the x-axis, percentage transmittance in color scale for the sample fabricated with static (left panel) and dynamic (right panel) spin coating.

These results provide a solid foundation for further investigation, including more detailed optomechanical analyses, advanced data processing, and the exploration of alternative material compositions or layer architectures. For these reasons, in the following chapters all samples presented will be fabricated using dynamic spin coating, while static spin coating will be abandoned.

2.3.3. Preliminary results on the removal of the substrate: Free standing stretchable mechanochromic DBRs

During the final months of the third year of my PhD, I co-supervised Camille Geliot, a visiting student from Sigma-Clermont University (France), who joined our laboratory as an Erasmus trainee to carry out her internship project. The objective of her work was the fabrication of free-

standing stretchable DBRs, that is, structures without the supporting elastic thick layer described above. I worked specifically on the design strategy for this new architecture. To obtain a truly free-standing structure, it was necessary to substantially increase the overall thickness, both to facilitate the peeling-off process and to allow subsequent handling of the sensor without risking mechanical failure. For this reason, in this phase we employed a very high number of layers (up to 30) and used the lowest achievable spinning speed to deposit layers as thick as possible. This was a three-month project; therefore, although significant progress was made, the results obtained are still preliminary and require further analysis. They are presented here to illustrate how the optimization of the fabrication process, initiated with the first sample generation discussed earlier in the chapter, was successfully extended to an even more challenging structure. While the free-standing DBR may appear simpler due to the absence of the supporting layer, it is in reality considerably more difficult to fabricate and to characterize. We fabricated two batches of samples, one consisting of 20 layers and the other 30 layers. To enable a direct comparison with the substrate-supported structures, each batch included one sample deposited on a substrate and one free-standing sample. Figure 2.13 reports the characterization of the 20-layer batch. Figure 2.13a and Figure 2.13b show the reflectance spectra, measured in nine distinct points of the supported and free-standing samples, respectively. In both cases, three diffraction orders of the PBG are clearly visible. For the substrate-supported sample (Figure 2.13a), the first-order PBG appears at ~ 845 nm, the second order at ~ 425 nm, and the third order at ~ 231 nm. Interference fringes are also visible in the background, indicating good optical quality of the multilayer. Moreover, the strong overlap of the spectra measured at different positions confirms a high degree of surface homogeneity. For the free-standing sample (Figure 2.13b), the spectral features are similar with a small hypsochromic shift: the first-order PBG is located at ~ 822 nm, the second at ~ 416 nm, and the third at ~ 229 nm. Interference fringes are again visible, and spectra show good overlap except for position 5, corresponding to the center of the sample, an area typically more affected by the fabrication procedure, as previously discussed. Overall, these results indicate that, at this stage, the absence of the substrate does not significantly influence the optical response of the samples. Encouraged by these findings, we peeled off the two samples and measured their mechano-optical response. Figure 2.13c and Figure 2.13d present the resulting color maps for the supported and free-standing samples, respectively, with strain reported on the y-axis for elongation (lower region) and contraction (upper region), wavelength on the x-axis, and reflectance represented by the color

scale. In both samples, the first and second diffraction orders of the PBG appear as bluish bands against a red background. The third-order PBG is not visible because it lies outside the detection range of the spectrometer used for these measurements.

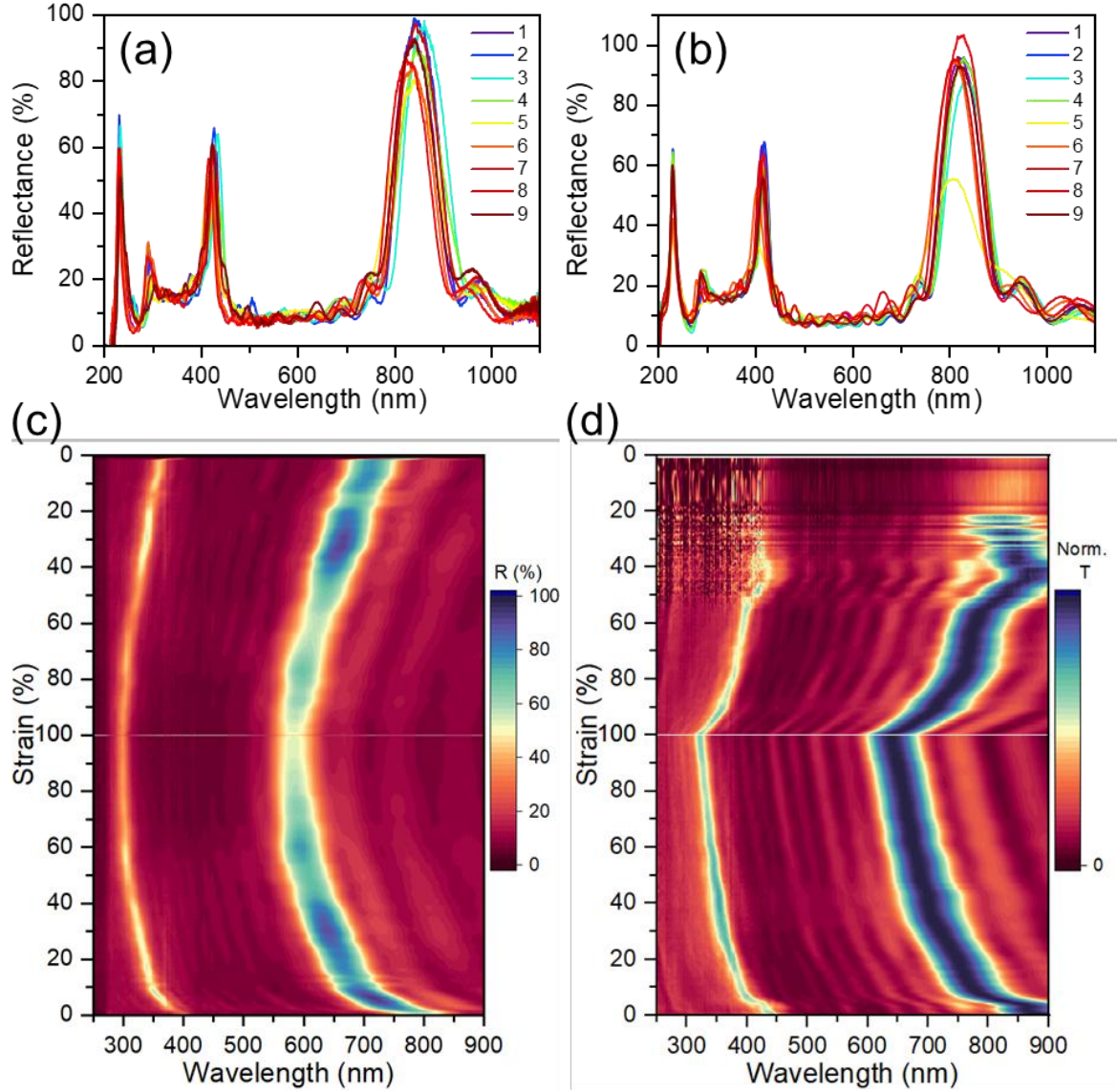


Figure 2.13: Reflectance spectra of the sample with substrate (a) and without substrate (b) collected in 9 distinct points. Color map with on the y axis the strain in the elongation (bottom part) and contraction (upper part) cycles in the x axis the wavelength of light and in color scale the reflectance for the sample without substrate (c) and with substrate (c).

In both cases, the PBG shifts toward shorter wavelengths during elongation and returns toward longer wavelengths during relaxation. For the substrate-supported sample, the PBG remains

clearly visible throughout both cycles. In contrast, the free-standing sample loses a well-defined PBG signal during the contraction phase at approximately 40% strain. This effect may be due to partial structural damage or to reduced mechanical resistance in the absence of the substrate, leading the film to fold during deformation. Since the measurement was performed in reflectance geometry, this folding likely caused a degradation of the optical signal due to reduced sample planarity and probably de-focusing. A difference in the slope of the PBG shift with respect to strain is also evident.

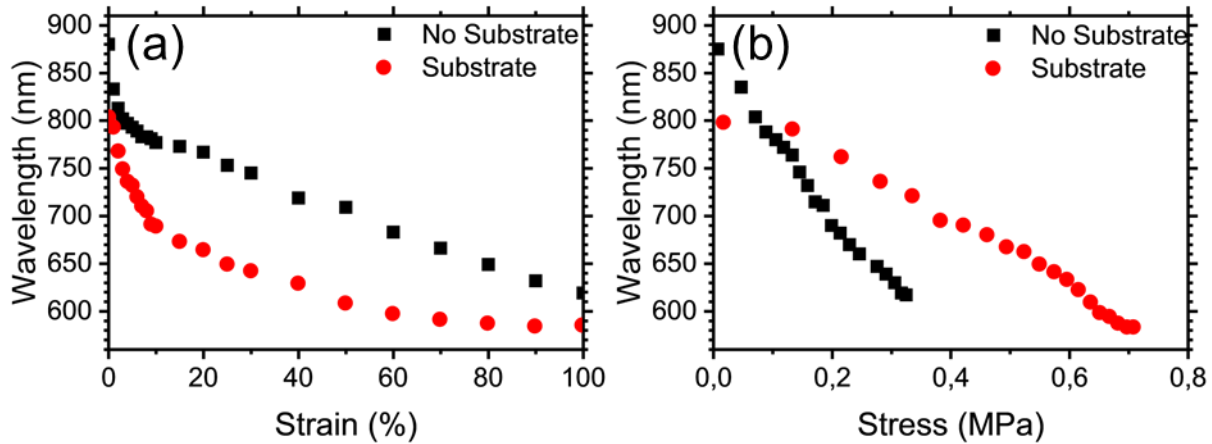


Figure 2.14: Scatter plot of the wavelength of the first order of diffraction of the PBG as a function of strain (a) and stress (b) for the sample without substrate (black squares) and with substrate (red dots).

To analyze this more quantitatively, Figure 2.14 compares the trend of the first-order PBG wavelength for the free-standing sample and the substrate-supported sample. Panel 13a reports the PBG wavelength as a function of strain, while panel b shows the same quantity plotted against stress. In both cases, only the elongation cycle is considered. In panel 13a, both samples display the expected blue shift of the PBG with increasing strain, consistent with the progressive reduction of the optical thickness of the layers during elongation. However, the two curves differ markedly in slope. The free-standing structure exhibits a much steeper wavelength decrease at low strain values (up to $\sim 10\%$), followed by a smoother decline at higher strains. In contrast, the substrate-supported sample shows a more gradual and uniform decrease over the entire strain range, reflecting a more distributed mechanical deformation. In Figure 2.14b, where the PBG shift is plotted as a function of stress, the distinction between the two samples becomes even clearer. Both trends decrease approximately linearly with increasing stress, yet the slopes differ significantly.

This is highlighted by the maximum stress each structure is able to sustain: approximately 0.4 MPa for the free-standing sample and about 0.7 MPa for the supported one. This indicates that the free-standing architecture withstands lower stresses before failure, whereas the presence of the substrate enhances the mechanical robustness of the multilayer. The reduced slope of the supported sample reflects the mechanical constraint imposed by the substrate, which increases the apparent stiffness of the system and limits the optical response for a given applied stress. Conversely, the free-standing multilayer translates smaller stresses into larger structural deformations, yielding a more pronounced spectral shift.

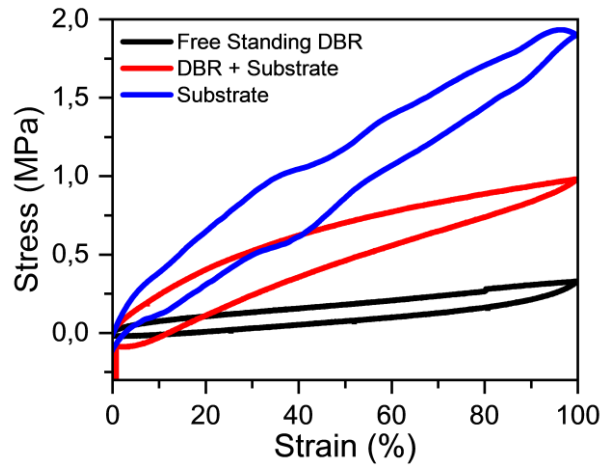


Figure 2.15: Stress vs strain curves of substrate (blue curves), free-standing multilayer (black curves) and substrate-supported multilayer (red curves).

We also decided to analyze the mechanical properties of the two samples and to compare them to the ones of the bare substrate. Figure 2.15 reports the mechanical stress vs strain curves of three systems: the bare substrate (blue curves), the free-standing multilayer (without substrate, black curves), and the substrate-supported multilayer (red curves) for the elongation and contraction cycles. The three curves clearly exhibit different slopes, reflecting distinct stiffnesses. The bare substrate shows the steepest slope and is therefore the stiffest structure, while the free-standing DBR displays the lowest slope, indicating that it is the most compliant and deformable. As expected, the supported DBR lies between these two extremes: its mechanical response is dominated by the substrate at low strains, but it remains slightly softer than the substrate alone due to the contribution of the elastomeric multilayer. This behavior confirms that the substrate dictates the apparent mechanical properties of the supported system, whereas the free-standing DBR reveals the intrinsic softness of the multilayer. Further data elaboration could enable independent

estimation of the Young's modulus and optical Poisson's ratio of the DBR itself. These values cannot be extracted from the supported samples, since, as shown in previous sections, their mechanical response is essentially governed by the substrate.

2.4. Conclusions

This work demonstrates the effective use of thermoplastic perfluorinated polymers in combination with commercially available styrene-based block copolymers as elastic constituents for the fabrication of mechanochromic photonic sensors with tunable mechanical properties, further refined through the integration of three distinct elastomeric substrates. The structures are fabricated via a spin-coating-based approach that avoids any cross-linking steps, thereby streamlining the processing workflow. The resulting distributed Bragg reflectors (DBRs) exhibit a pronounced mechanochromic response, characterized by multiple photonic band gaps (PBGs) that induce spectrally dependent optical behavior across the visible region and extending into the telecommunication wavelength range. Following the realization of a first generation of stretchable DBRs, a second generation was developed by implementing a dynamic spin-coating process in combination with an alternative styrene-based thermoplastic material. This approach enabled a significant improvement in optical quality while also allowing the fabrication of a free-standing, substrate-free DBR sample, which will serve as a platform for further investigations. The fabricated sensor architectures display exceptional mechanical resilience, sustaining strains of up to 400%. A detailed analysis of the optical response under both loading and unloading conditions permitted a quantitative assessment of the mechanochromic behavior, providing phenomenological insights that are rarely reported in the literature. The system shows stable, fully reversible performance over repeated deformation cycles at 100% strain, underscoring its suitability for reliable and long-term optomechanical sensing. Importantly, the optical response remains consistent under mechanical deformation, effectively mitigating issues such as layer delamination or nanoscale structural failure. At low applied strains ($<20\%$), the mechanochromic sensitivity depends on the diffraction order under observation, with the photonic band gap exhibiting a linear spectral shift with strain, thereby enabling application-specific spectral tuning.

2.5. References

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3. Dual-Responsive Mechanochromic Architectures

Chapter at a Glance: Chapter 3 explores the integration of a supramolecular polyurethane incorporating 4,4'-methylenebis(cyclohexyl isocyanate) (HMDI) hard segments and a loop-forming mechanophore unit (Loop-HMDI-PU) with one-dimensional polymer-based distributed Bragg reflectors (DBRs) to create a hybrid mechanoresponsive system. The Loop-HMDI-PU material retains its distinctive dual excimer–monomer emission at thicknesses suitable for photonic integration, providing a reliable and reversible strain-dependent optical signal up to 100% deformation. The stretchable polymeric DBRs exhibit well-defined first- and second-order photonic bandgaps, high optical uniformity, and consistent performance under repeated strain, with reflectance measurements revealing significant and reversible blue shifts. When combined, the DBRs selectively modulate the mechanophore output: depending on orientation and applied strain, excimer emission is reduced or monomer emission enhanced, resulting in distinct strain-dependent fluorescence ratios. Two-dimensional spectral mapping confirms that the elastomeric DBR can act both as a spectral filter and as a reflective amplifier, with reversible modulation maintained throughout deformation cycles. This hybrid design enables sensitive, fully reversible optical strain readouts and introduces new strategies for tuning light–matter interactions in soft materials, highlighting potential applications in stress sensing, tunable light sources, and responsive coatings.

3.1. Introduction

A wide range of approaches have been pursued to realize such mechanoresponsive behavior. Early examples focused on conjugated polymers, in which mechanical perturbations affect the conformation of the polymer backbone, altering π -conjugation and consequently shifting optical spectra.^[1] Similarly, covalent mechanophores, molecular motifs embedded in polymer matrices that contain mechanically cleavable bonds, have been widely explored.^[2] Under sufficient strain or stress, these mechanophores undergo covalent bond scission, leading to irreversible changes in their electronic structure and associated optical properties.^[3] Although covalent mechanophores have provided fundamental insights into force-induced chemistry and enabled proof-of-principle stress-sensing applications, they suffer from intrinsic limitations that constrain their broader utility.^[4] In most cases, mechanical activation requires surpassing relatively high threshold forces, meaning that subtle deformations occurring at the onset of material fatigue may not be detected.^[5]

Furthermore, the bond-breaking process is often irreversible or only slowly reversible, necessitating external triggers such as UV light or heat to restore the mechanophore to its pristine state.^[6] To overcome these challenges, attention has increasingly shifted toward mechanoresponsive motifs based on non-covalent interactions.^[7, 8, 9, 10] Rather than relying on the scission of strong covalent bonds, these systems harness weak and reversible supramolecular forces, such as π - π stacking^[11], hydrogen bonding^[12], or host-guest interactions^[13], to achieve mechanically induced switching. A pioneering example is the use of excimer-forming dyes, such as cyano-substituted oligo(p-phenylene vinylene), which exhibit excimer-dominated emission in the aggregated state and monomer-dominated emission upon mechanical disruption.^[14] When incorporated into polyurethane matrices^[15], these dyes provide a clear, reversible color change under strain, establishing excimer-based mechanochromism as a viable design strategy. Building on this concept, more sophisticated supramolecular mechanophores have been developed. Rotaxane architectures containing reversibly separable quencher/emitter pairs^[16] and cyclophane mechanophores bearing excimer-forming pyrene dyes^[17] have demonstrated specific and instantaneous reversible mechanochromic responses. However, their practical implementation has been obstructed by synthetic complexity and limited scalability.^[18] To address these constraints, loop-forming mechanophores have emerged as an elegant and efficient alternative.^[19] By covalently linking two chromophores in a loop-like architecture, excimer interactions dominate in the relaxed state, while applied strain leads to loop unfolding and monomer emission.^[20] A notable example of this class is the loop-forming perylene diimide (PDI) mechanophore, which was recently incorporated into thermoplastic polyurethanes.^[9] In this context, we refer to a supramolecular polyurethane, known as Loop-HMDI-PU, which is based on 4,4'-methylenebis(cyclohexyl isocyanate) (HMDI) hard segments and functionalized with the loop-forming mechanophore unit (Figure 3.1).

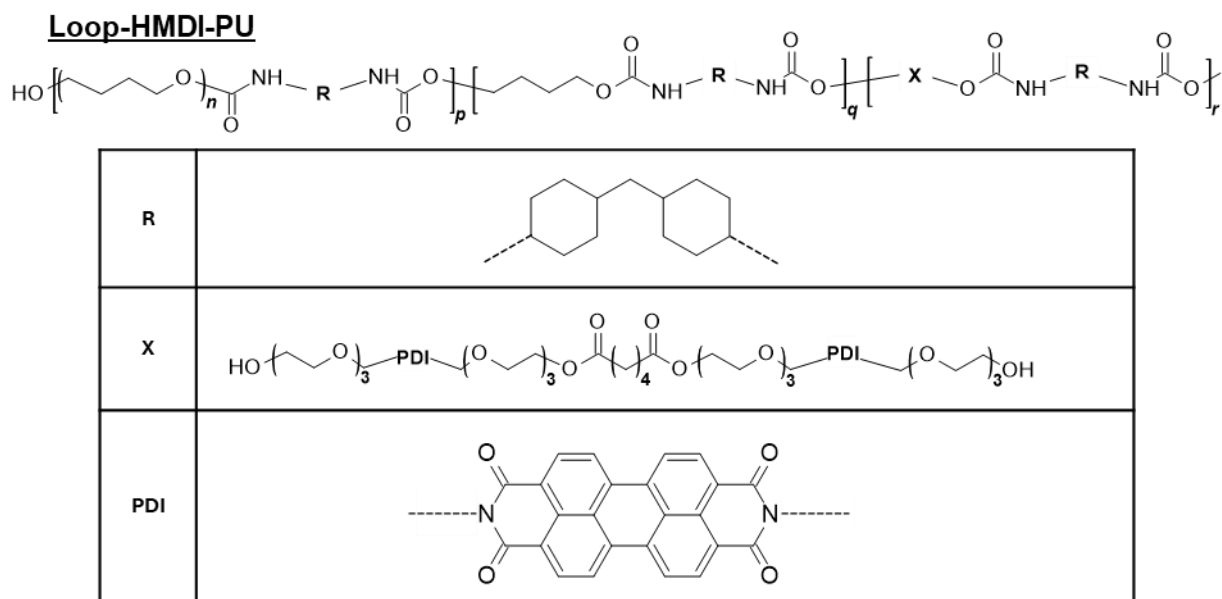


Figure 3.1: Molecular structure of the mechanophore Loop-HMDI-PU.

This motif combines several attractive features: straightforward synthesis in a few steps, reversible switching between excimer and monomer emission, and seamless integration into polymer backbones.^[20] In the absence of stress, the perylene dyes interact strongly within the loop, producing orange excimer emission. Upon elongation, the loops unfold, and the dyes dissociate, yielding green monomer emission, as shown in Figure 3.2. The color transition was continuous and correlated quantitatively with the applied strain, enabling real-time optical reporting of deformation. Importantly, this process is reversible, allowing repeated cycling without permanent material alteration. Such non-sacrificial mechanophores represent a new generation of stress-sensitive motifs, ideal for dynamic sensing and for integration into hybrid material systems.^[9]

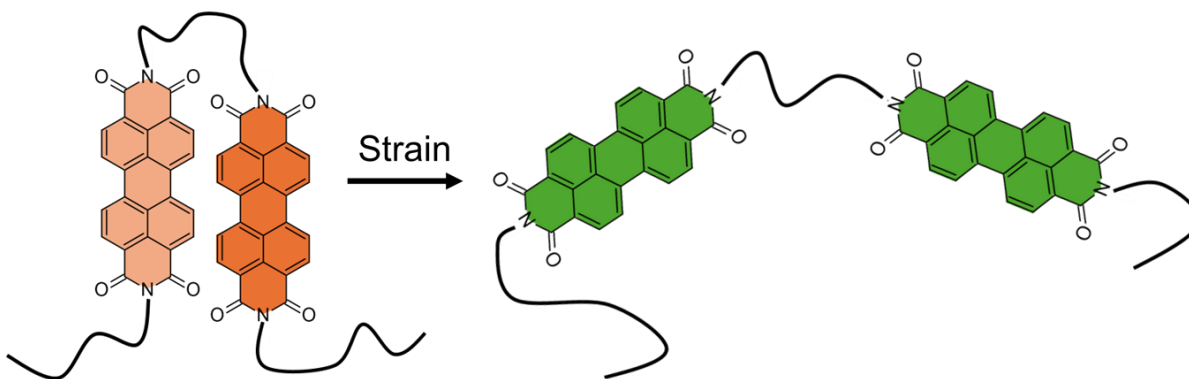


Figure 3.2: Loop-formation-related mechanochromic mechanism of the Loop-HMDI-PU

In parallel with the progress in molecular mechanophores, photonic crystals (PhCs) have emerged as an entirely different but complementary platform for mechanochromism.^[21, 22] Among the various architectures, one-dimensional multilayered PhCs, commonly known as distributed Bragg reflectors (DBRs), are particularly appealing because of their relative simplicity and well-defined optical response. Mechanical deformation alters the thickness and periodicity of the layers, thereby shifting the PBG and producing a measurable chromatic change. DBRs fabricated from elastomeric polymers combine the optical functionality of photonic crystals with the mechanical flexibility required for mechanochromic applications.^[23] Given these complementary advances, the molecular sensitivity and reversibility of non-covalent mechanophores, and the structural tunability and optical amplification of DBRs, an obvious yet underexplored opportunity lies in their integration, and hybrid materials that couple mechanochromic mechanophores with a photonic structure can exhibit responses inaccessible to either component alone. Specifically, the DBR can act as a spectral filter, selectively suppressing or amplifying the mechanophore emission depending on the wavelength alignment. Conversely, the intrinsic luminescence switching of the mechanophore provides an internal light source, the output of which is dynamically modulated by the DBR. Together, these effects establish a synergistic platform in which molecular and structural mechanochromism reinforce each other. In this study, we report the fabrication and characterization of such a hybrid system: a polymer-based stretchable DBR fabricated on top of a film of looped hexamethylene diisocyanate (Loop-HMDI)-PU mechanophores. We demonstrated that the mechanophore retains its characteristic dual emission (excimer and monomer) even in

films with thickness suitable for this integration. High-quality polymeric DBRs with well-defined and uniform photonic bandgaps were fabricated as described in Chapter 2 starting from a fluoroelastomer (PFR 94) and a styrene-ethylene-butylene-styrene thermoplastic elastomer grafted with maleic anhydride (SEBS-MAH). Integration with the mechanophore resulted in a multilayer architecture in which fluorescence was selectively modulated: the DBR could either suppress the excimer emission or enhance the monomer emission, depending on the position of the Loop-HMDI-PU film relative to the collection probe and the applied strain. For clarity, we define two configurations, referred to as Loop DOWN (probe facing the Loop-HMDI-PU layer) and Loop UP (probe facing the DBR), as illustrated in Figure 3.3. Strain-dependent spectroscopic analyses revealed that the DBR alternately functions as a spectral filter or reflective amplifier with reversible effects. This coupling of molecular mechanochromic motifs with stretchable photonic structures establishes a versatile strategy for engineering mechano-responsive materials, enabling multifunctional devices that both sense mechanical stress and manipulate light.

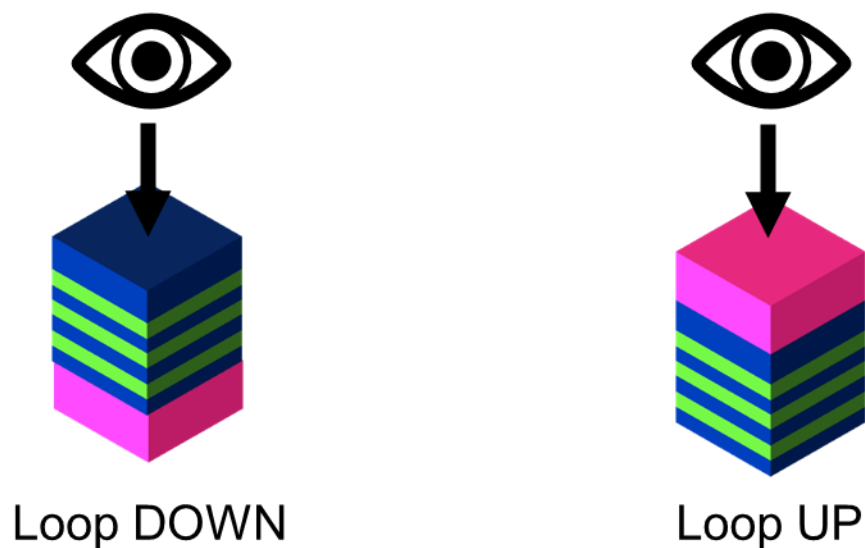


Figure 3.3: Schematic of the Loop DOWN and Loop UP configurations.

3.2. Materials and Methods

3.2.1. Sample Preparation

Loop-HMDI-PU Support: The DBRs were fabricated on glass substrates ($25 \times 25 \times 1 \text{ mm}^3$), which were first coated with a thick layer of polyurethane serving as a flexible support. This elastic base was prepared by drop-casting 500 μL of a toluene solution (30 mg mL^{-1}) of Loop-HMDI-PU.

DBRs: DBRs were constructed using a dynamic spin-coating method by applying alternating layers of polymer solutions. Tecnoflon PFR94 (SYENSQO) was selected as the low-refractive-index component ($n \approx 1.32$), while the high-refractive-index material ($n \approx 1.5$) was a styrene-butylene-ethylene-styrene copolymer functionalized with maleic anhydride (SEBS-MAH). Specifically, Tecnoflon was dissolved in Galden HT 135 (Solvay Specialty Polymers S.p.A.) at a concentration of 60 mg mL^{-1} (Solvay Specialty Polymers S.p.A.), while SEBS-MAH was dissolved in toluene at 30 mg mL^{-1} . $100 \text{ }\mu\text{L}$ of each polymer solution was sequentially deposited in alternating layers to build the final multilayer structure. Prior to each SEBS-MAH layer deposition, low-pressure cold plasma treatment (Zepto, Diener Electronic) was applied to the surface to enhance the wettability of the PFR layer, as previously described.^[23, 24] Tecnoflon PFR94 was used in its uncrosslinked form. Each DBR sample comprised 10 bilayers (BLs). The complete scheme for the preparation of the samples is shown in Figure A1.3.

3.2.2. Characterization

Normal-incidence reflectance spectra were recorded using a custom-built optical fiber-based setup. A light beam from a tungsten-halogen light source (AvaLight-CAL (-Mini)) was irradiated onto the DBR surface using a UV-vis-optical fiber probe (Avantes QP230-2-XSR). The signal was then sent to a UV-vis detector (Ocean Optics QEPro) for analysis.

Prior to mechanical characterization, each DBR grown on an elastomeric support film was removed from the glass substrate. The optomechanical characterization of the samples was performed using a custom-built optical fiber setup integrated into a tensile machine on rectangular samples with dimensions of $20 \text{ mm} \times 5.5 \text{ mm} \times 0.05 \text{ mm}$ (length $\times$ width $\times$ thickness). The experiments were carried out on a Linkam TST350 microtensile stage equipped with a 20 N load cell at a strain rate of $100 \text{ }\mu\text{m s}^{-1}$, with a maximum strain value of 100%. Fluorescence changes in the polymer films as a function of mechanical strain were recorded using an Ocean Optics QEPro spectrometer connected to an Ocean Optics LS-450 LED light source with an excitation wavelength of $\lambda_{\text{ex}} = 470 \text{ nm}$, an optical fiber (Avantes FCR-7UVIR200-2-ME) and a long pass 520 nm filter for the collection (Thorlabs). The measurement set up is shown in Figure A1.4.

3.3. Results and Discussion

To determine whether the characteristic spectral fingerprint of Loop-HMDI-PU mechanophores, comprising both folded (excimer) and unfolded (monomer) emission signatures, was retained at a

film thickness of approximately 50 μm , We first characterized the drop-cast monolayer film. The photoluminescence spectra, presented in Figure 3.4a, reveal three principal emission peaks centered at 525, 574, and 623 nm. The most intense peak at 525 nm corresponds to the monomeric form (unfolded mechanophore). Despite its intensity, it will not be further discussed due to significant self-absorption effects.^[9] The peak at 574 nm is also attributed to the monomeric form. Notably, the least intense peak at 623 nm is assigned to the excimer emission, indicative of the folded mechanophore conformation. This unexpectedly low excimer signal may be attributed to the fabrication conditions, which diverge significantly from previously reported examples.^[8, 9] In our case, the drop-casting procedure is performed directly onto the glass substrate used for the DBR fabrication, whereas in the literature drop casting is typically an intermediate step followed by hot pressing to achieve a controlled film thickness. Despite the reduced presence of the folded form, we proceeded with optomechanical characterization to evaluate whether the mechanoresponsive functionality was retained. Fluorescence measurements were conducted under varying strain conditions up to a deformation of 100%, and the resulting data are shown in Figure 3.4b. Specifically, in order to quantify the response of the excimer with respect to the monomer, we monitored the ratio between the emission intensities at 574 nm (monomer, internal standard) and 623 nm (excimer), a metric commonly employed in the literature to quantify the mechanophore response.^[8, 9] As said before, the 525 nm peak was excluded from the analysis owing to its susceptibility to self-absorption artifacts. The fluorescence ratio exhibited a marked initial increase, likely reflecting the release of slack within the sample, followed by a consistent upward trend as the strain increased, we decided to exclude the first and last 10% of strain from our analysis due to its higher susceptibility to this deformation effects. While the overall behavior aligns with previously reported mechanochromic systems, the absolute values of the ratio remain higher, likely reflecting the diminished population of folded mechanophores (excimer form) in the film. In previously reported systems, the ratio usually falls around 1.^[9]

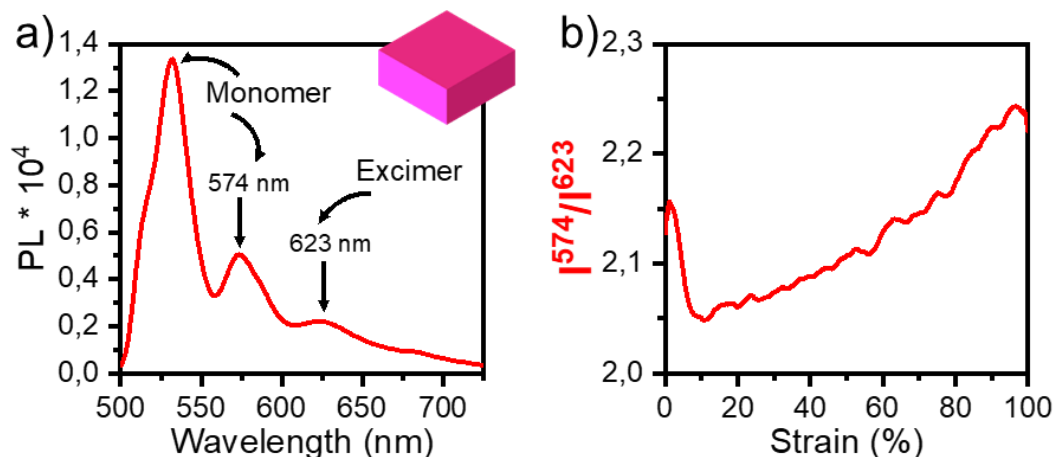


Figure 3.4 a): Fluorescence spectrum of the single Loop-HMDI-PU film, showing three distinct fluorescence peaks: two at lower wavelengths associated with the monomeric (unfolded) form (525 and 574 nm) and one at a higher wavelength corresponding to the excimer (folded) form (623 nm). b): Ratio between the fluorescence intensity of the monomer peak (574 nm) and the excimer peak (623 nm) plotted as a function of the applied strain (percentage of elongation).

After verifying that the characteristic spectral fingerprint of Loop-HMDI-PU, comprising both folded (excimer) and unfolded (monomer) emission signatures, was retained even with this simpler fabrication procedure, we proceeded with the fabrication of a distributed Bragg reflector (DBR), employing the Loop-HMDI-PU film as the substrate to obtain a multilayered structure similar to the one reported in Chapter 2.^[23] A schematic of the complete multilayer architecture is presented in the inset of Figure 3.5a. The fabrication protocol followed the procedure detailed in the Materials and Methods section and was previously validated in Chapter 2. The reflectance spectrum of the resulting DBR, acquired at normal incidence and measured across nine distinct points on the sample, is shown in Figure 3.5a. The spectrum reveals two prominent peaks corresponding to the photonic band gaps (PBGs) of the multilayer structure: the first-order PBG centered near 740 nm, and a second-order PBG appearing at approximately half that wavelength, near 370 nm. Additionally, interference fringes were visible in the background, arising from coherent light transmission through the entire structure, indicative of high optical quality and thickness uniformity. To assess spatial homogeneity, reflectance measurements were performed at nine points on the sample. The resulting spectra exhibited a strong overlap, confirming good uniformity throughout the film. A slight deviation was observed in the violet spectrum, corresponding to the central region of the sample. This discrepancy is consistent with well-known

limitations of dynamic spin-coating techniques, where the center is often subject to fabrication-induced defects (position where the drop is released), as previously reported.^[25]

The multilayer was then carefully detached from the rigid glass substrate used during fabrication and integrated into a custom-built tensile setup equipped with an optical fiber-based reflectance measurement system, as described in the Materials and Methods section. The reflectance was recorded during both the elongation and relaxation cycles up to a 100% deformation, and the collected spectra are presented in the form of a colormap, where the strain percentage is plotted along the y-axis, the wavelength along the x-axis, and the reflectance intensity is represented in the color scale (Figure 3.5b). The first-order PBG is clearly identifiable as a blue region against a red background, with surrounding orange bands corresponding to the interference fringe pattern previously observed in the static spectrum. A fraction of the second-order PBG is also discernible; however, it falls outside the scope of the present discussion and will not be considered further, as during stretching it rapidly shifts beyond the measurable spectral range (350 nm – 1100 nm) and will therefore be excluded from subsequent analyses. With increasing strain, the first-order PBG exhibited a pronounced blue shift, transitioning from 740 nm to approximately 550 nm at maximum elongation, and subsequently returning to ~720 nm during relaxation. This reversible shift is consistent with theoretical predictions and prior experimental observations^[23], confirming the dynamic tunability of this system. Furthermore, the fringes shifted toward shorter wavelengths during deformation, indicating that the optical integrity of the multilayer was preserved throughout the mechanical cycle.

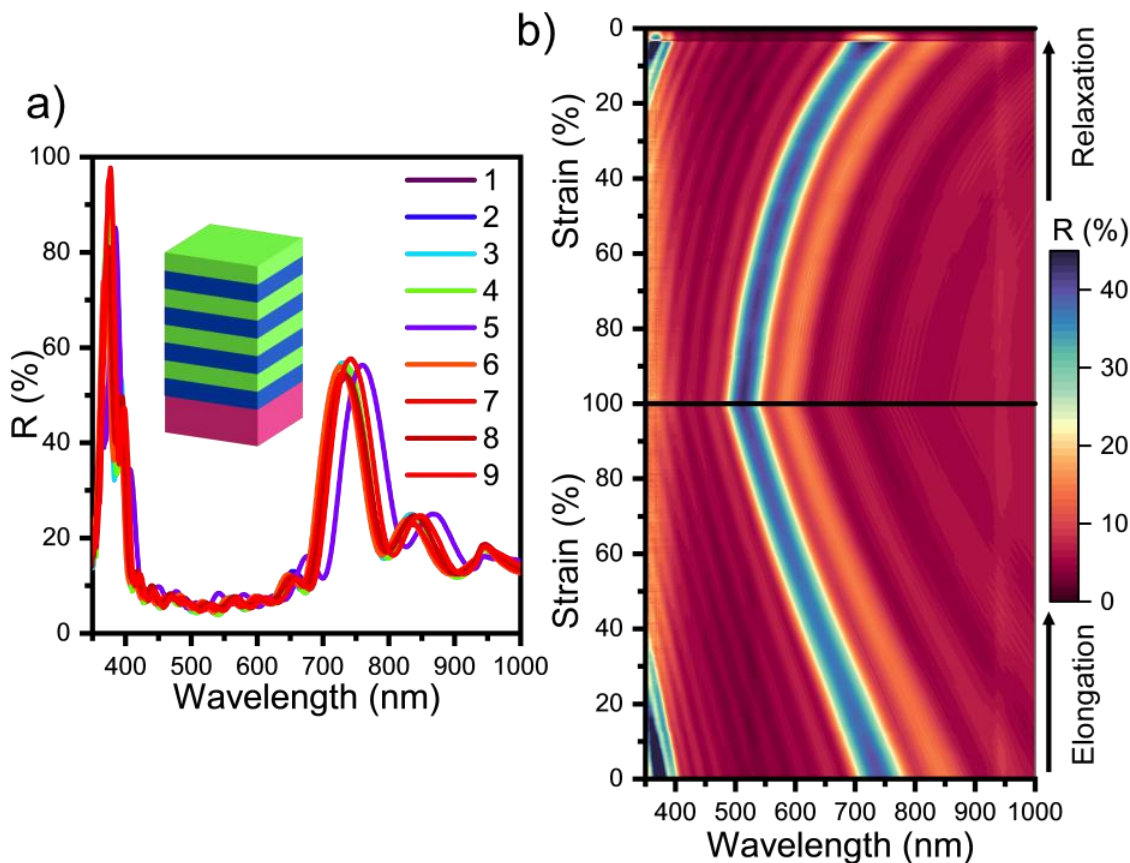


Figure 3.5: a): Reflectance spectra of the DBR structure measured at nine distinct locations across the sample. The inset illustrates a schematic of the multilayer architecture (not to scale and not representing the exact number of bilayers). b): Optomechanical reflectance measurements presented as a color map, with the strain percentage from the elongation and relaxation cycles on the y-axis, wavelength on the x-axis, and reflectance intensity in the color scale.

Following the optical characterization of the DBR, we investigated the influence of the photonic bandgap on the mechanoresponsive behavior of the mechanophore. Using the same custom-built optical setup, we measured the fluorescence of the complete multilayer architecture under varying strain conditions, up to a maximum of 100%, as in Chapter 2.^[23] Expecting distinct responses from the two sides of the multilayer, the measurements were conducted by positioning the probe in both positions, facing the DBR (Loop DOWN) and the Loop film (Loop UP) (Figure 3.3). We calculated the fluorescence intensity ratio between the monomer and excimer emissions and plotted this ratio as a function of strain during both elongation (Figure 3.6a and Figure 3.8a) and relaxation (Figure

3.6b and Figure 3.8b) cycles, as shown by the red curves. For reference, the corresponding trend from the drop-cast Loop-HMDI-PU single film PL ratio spectra is included in both elongation plots as a light-grey curve. To directly correlate the mechanochromic response with the optical properties of the DBR, the wavelength shift of the first-order PBG is represented as a scatter plot against the strain in the elongation cycle (black squares). This allows the reader to simultaneously track the evolution of the PBG and compare it with the fluorescence behavior of the mechanophore.

For clarity, the discussion will begin with the measurements obtained from the Loop DOWN configuration of the sample (Figure 3.6a and Figure 3.6b) during both elongation and relaxation. In the elongation cycle, we observed a general increasing trend in the monomer-to-excimer ratio, consistent with the behavior reported in Figure 3.4. However, a notable difference emerged: a broad peak appeared between 30% and 70% strain, reaching a maximum ratio (minimum excimer signal) of approximately 3.5. During the relaxation cycle, the ratio exhibited a decreasing trend, consistent with the behavior reported in previous studies.^[9] Interestingly, a similar peak was observed in the same strain range (70% to 30%), again reaching a maximum ratio of 3.5. At the end of the relaxation curve, a slight increase in the ratio was observed, likely resulting from the release of residual slack in the sample; however, as mentioned previously, this range of strains was excluded from the analysis.

producing a comparable increase in the fluorescence ratio. To deepen the interpretation of the fluorescence ratio behavior, in Figure 3.6, we present the original normalized photoluminescence spectra of the sample at three representative strain values: 20% (red curve), 44% (green curve), and 80% (violet curve) for the elongation cycle (Figure 3.7). These spectra correspond to the region preceding the peak in the fluorescence ratio, the point of maximum ratio, and the final stage of the elongation cycle. At 20% strain, the spectrum exhibited the canonical three emission peaks characteristic of the Loop-HMDI-PU mechanophore, with distinct contributions from both the monomeric (unfolded) and excimer (folded) forms. At 44% strain, the peak in the fluorescence ratio, the excimer emission at ~ 623 nm, was markedly suppressed, leaving only the two monomer-related peaks clearly discernible. This spectral attenuation is consistent with the photonic band gap overlapping with the excimer emission, effectively filtering it out. At 80% strain, the spectrum was dominated by a single monomeric peak at ~ 525 nm, likely due to limitations in signal acquisition or reduced emission intensity at higher deformation levels.

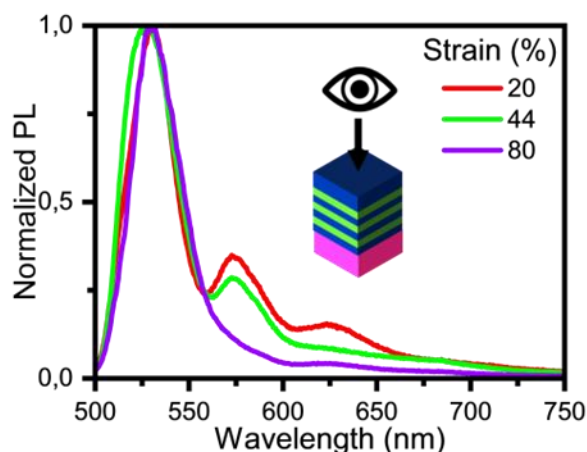


Figure 3.7: Normalized photoluminescence spectra of the sample at three representative strain values: 20% (red curve), 44% (green curve), and 80% (violet curve) for the elongation cycle

Having clarified the behavior from this side of the sample, we proceeded to analyze the measurements acquired from the Loop UP of the sample, where obviously the Loop-HMDI-PU layer faces the probe of collection (Figure 3.8a and Figure 3.8b). In the elongation cycle, the fluorescence ratio exhibited a general increasing trend, with distinct minima and maxima between 30% and 80% strain. The ratio decreased to a minimum of ~ 1.5 and increased to a maximum of ~ 4.4 . This pattern is mirrored in the relaxation cycle, where the maximum precedes the minimum within the same strain range, again reaching values of ~ 4.4 and ~ 1.5 , respectively. As in the

previous configuration, we included both the reference curve from the single Loop-HMDI-PU film and the scatter plot of the first-order PBG position to facilitate interpretation. During the elongation cycle, the first peak in the ratio occurred at ~44% strain, where the first-order PBG was again centered near ~625 nm, matching the excimer emission. However, in this configuration, the mechanophore layer is directly exposed to the probe. Thus, when the PBG overlaps with the excimer emission, the DBR reflects this light toward the detector, enhancing the measured excimer intensity and consequently decreasing the fluorescence ratio. The second peak in the ratio appears at ~64% strain, where the first-order PBG shifts to ~570 nm, matching the monomer emission. In this case, the DBR reflected the monomer emission back to the probe, resulting in a pronounced increase in the fluorescence ratio. Notably, this ratio was higher than that observed on the Loop DOWN configuration of the sample. This is attributed to the fact that, in Loop UP configuration, the DBR directly enhances the monomer signal (higher reflectance toward the detection), whereas in the Loop DOWN configuration, the ratio increase was driven by the suppression of the excimer emission (excimer signal reflected far from the detection).

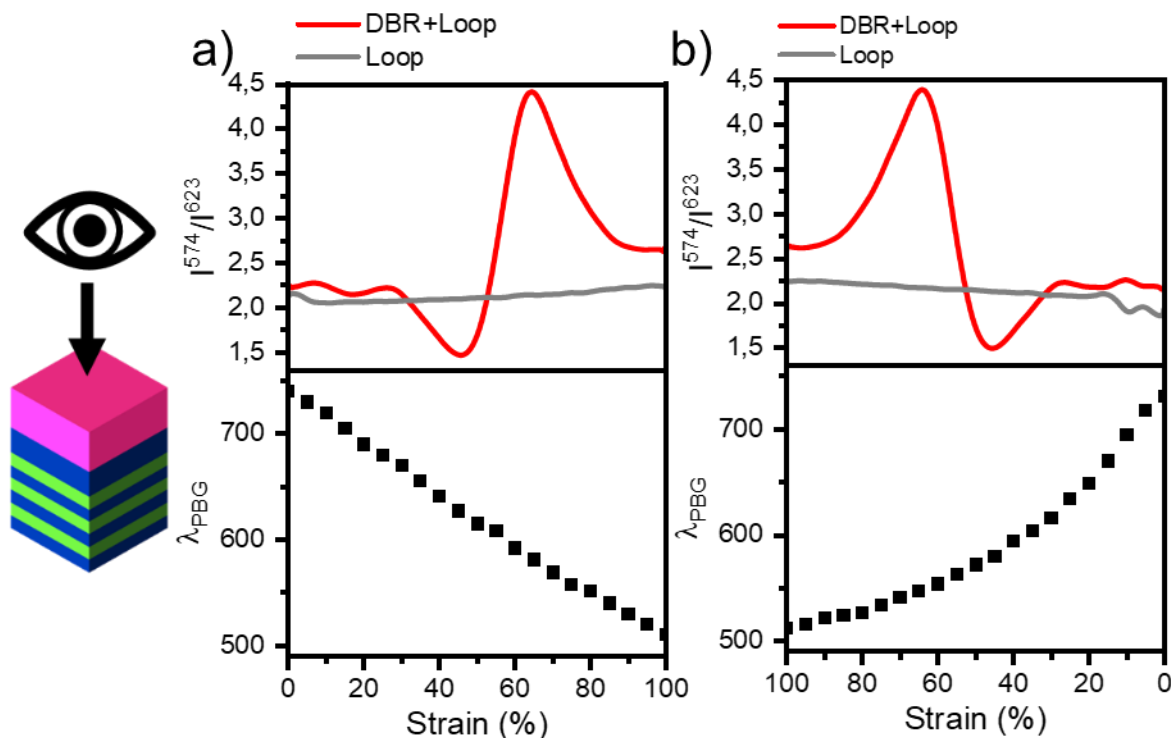


Figure 3.8: Inset: representation of the Loop UP probing configuration. Main panel: monomer-to-excimer intensity ratio for the DBR + Loop structure (red curve) and the Loop single film (light gray curve), with a scatter plot (blue squares) showing the photonic bandgap (PBG) wavelength as a function of strain for (a) elongation and (b) relaxation cycles.

To further elucidate the fluorescence ratio behavior observed in Figure 3.8, we present in Figure 3.9 the original normalized photoluminescence spectra of the sample at four representative strain levels during the elongation cycle: 20% (red curve), 44% (green curve), 64% (blue curve), and 98% (violet curve). These spectra correspond to the region preceding the minimum fluorescence ratio, the point of minimum ratio, the point of maximum ratio, and the final stage of elongation. At 20% strain, the spectrum displays the canonical three emission peaks characteristic of the Loop-HMDI-PU mechanophore, with distinct contributions from both monomeric (unfolded) and excimer (folded) forms. At a strain of 44%, which corresponds to the minimum in the fluorescence ratio, the excimer emission at ~ 623 nm is markedly enhanced, whereas the two monomer-related peaks remain visible. This enhancement is consistent with the photonic bandgap overlapping with the excimer emission, thereby reflecting it back toward the detection probe and consequently precisely amplifying its measured intensity. At 64% strain, which corresponds to the maximum

fluorescence ratio, the monomer emission at 574 nm is significantly enhanced, whereas the excimer peak appears suppressed. However, this apparent suppression is due to the presence of the DBR, rather than the true absence of the folded form. The observed enhancement is again attributable to the photonic bandgap overlapping with the monomer emission, resulting in increased back-reflection toward the probe. At 98% strain, the spectrum was dominated by the monomeric peak at ~525 nm, likely due to limitations in signal acquisition or reduced overall emission intensity at high deformation levels. The other two peaks were faintly discernible in the background.

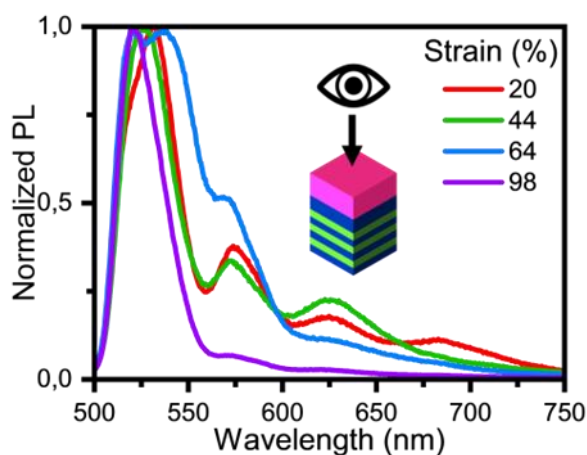


Figure 3.9: Normalized photoluminescence spectra of the sample at four representative strain levels during the elongation cycle: 20% (red curve), 44% (green curve), 64% (blue curve), and 98% (violet curve).

To gain deeper insights into the role of the multilayer structure in the fluorescence response, we calculated the spectral ratio between the emission of the multilayer on top of the Loop-HMDI-PU film and that of the Loop-HMDI-PU single film alone as a function of the applied strain. The calculation was performed over a complete elongation cycle, considering the fluorescence collected from both sides of the multilayer: the Loop DOWN configuration (Figure 3.10a) and the Loop UP configuration (Figure 3.10b). The results are presented as two-dimensional colormaps, where the x-axis corresponds to the fluorescence emission spectrum, the y-axis to the applied strain percentage, and the color scale to the spectral ratio between the multilayer and single-film reference. Values above 1 are displayed in green, values below 1 are displayed in red, and values equal to 1 are displayed in white. This visualization enables the direct identification of spectral

regions where the DBR either enhances (above 1) or suppresses (below 1) the emission of the mechanophore.

In the DBR-side configuration (Figure 3.10a), the color map is dominated by extended red regions. In particular, a pronounced red band emerged in the 600–700 nm spectral window (excimer emission) for strain values between 30% and 80%, indicating a systematic suppression of fluorescence in this area. This behavior is consistent with the filtering effect of the DBR, which selectively inhibits the transmission of emitted light at specific wavelengths. When observed from the Loop-HMDI-PU side (Figure 3.10b), the colormap revealed a prevalence of green regions corresponding to enhanced fluorescence in the same spectral region. Two major green bands were clearly distinguished across a mixed red–white background, with the most intense enhancement observed between 600 and 650 nm and strain values of 30–60%. This trend is consistent with the DBR acting as a reflective element that amplifies mechanophore emission. Overall, this spectral ratio analysis provides direct evidence of the dual role of the DBR: as a selective optical filter when probed from the DBR side and as a mirror-like amplifier when probed from the Loop-HMDI-PU side. Such dual functionality highlights the strong interplay between photonic structuring and mechanophore emission, reinforcing the appeal of integrated multilayer platforms as a fertile ground for the development of novel stimuli-responsive technologies and advanced sensing applications.

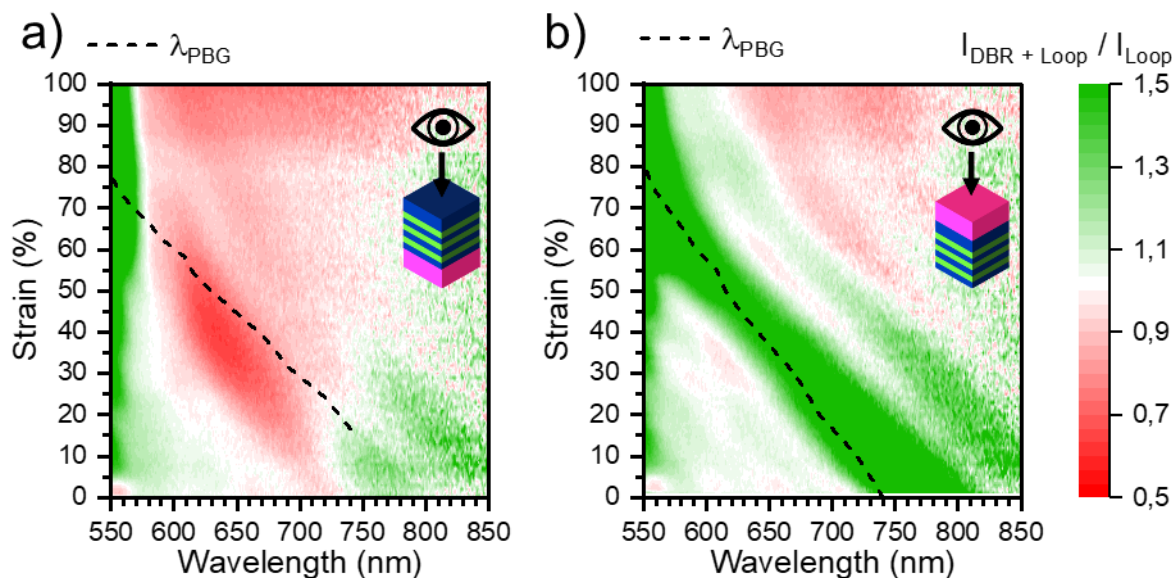


Figure 3.10: Spectral ratio between the data of the multilayer system and the single Loop-HMDI-PU film in the form of color maps with the strain of the elongation cycle in the y-axis, wavelength in the x-axis, and ratio in the color scale. Green area ratio >1 , white area ratio $=1$, and red area ratio <1 . Top panel: Results of the calculations for the DBR-facing side. Bottom panel: Results of the calculations for the Loop-HMDI-PU-facing side.

3.4. Conclusions

In this chapter, we have demonstrated the feasibility and success of integrating a supramolecular loop mechanophore (Loop-HMDI-PU) with a polymer-based stretchable distributed Bragg reflector (DBR) to establish a hybrid mechanoresponsive platform. The mechanophore maintains its dual excimer–monomer emission at thicknesses compatible with the photonic structure, while the engineered stretchable DBR offers dynamically tunable photonic band gaps with excellent optical uniformity. When combined, these components facilitate reversible, strain-dependent modulation of fluorescence, with the DBR serving as either a spectral filter or a reflective amplifier, contingent upon the relative orientation. These findings underscore a potent strategy for coupling molecular-scale mechanochromic motifs with mechanochromic photonic architectures to achieve selective suppression or amplification of mechanophore emission without chemical modification. Beyond affirming the robustness and versatility of Loop-HMDI-PU integrated with engineered elastomeric DBRs, this study establishes a broadly applicable design principle for mechanoresponsive materials. The capability to engineer optical responses through the interplay

of supramolecular mechanophores and engineered photonic multilayers presents opportunities for multifunctional devices in strain sensing, tunable light sources, and responsive coatings. More broadly, this study highlights the value of hybrid molecular–photonic systems as a platform for advancing soft functional materials, where mechanical input directly dictates optical output.

3.5. References

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4. Stretchable Planar Microcavities

Chapter at a Glance: Chapter 4 presents the design and experimental characterization of stretchable planar microcavities (MCs) embedding active emitters within the defect layer. Polymer-based DBRs were used to form the cavities, combining optical functionality with mechanical flexibility, enabling tunable photonic properties under external deformation. Two representative fluorophores were investigated. The first system employed the conjugated polymer F8BT blended with SEBS-MAH, which confirmed the expected photonic behavior, including the presence of photonic band gaps and multiple cavity modes. When detached from the substrate and subjected to uniaxial strain up to 100%, both transmittance and photoluminescence measurements revealed clear and reversible optical modulation, demonstrating that the mechano-optical response originates from the cavity rather than the intrinsic emitter properties. The second system focused on spiropyran (SP), a mechanochromic molecule typically exhibiting binary color switching. Integration into the microcavity suggested that the photonic environment could qualitatively influence its functionality, potentially enabling continuous spectral tunability over approximately 50 nm with reversible and low-hysteresis behavior. Although these observations are preliminary and require further systematic investigation, they indicate that elastomeric MCs may enhance or even create new optical functionalities in embedded emitters. These cautious results highlight the prospective value of stretchable MCs as versatile platforms for exploring strain-dependent photonic phenomena and developing future optomechanical applications, while emphasizing that additional studies are necessary to fully confirm these effects.

4.1. Introduction

As already pointed out, planar MCs are optical nanostructures made by two highly reflective mirrors, often realized as DBRs,. The light emitted by the cavity layer is reflected back and forth by the two side mirrors (suitable spectrally tuned) giving rise to unusual properties. For instance, light can be spatially confined within the cavity thus allowing photons to interact with the excited states of the fluorophore. Two regimes are possible: the weak-coupling where the life-time the emitter can be modified (with respect to that of the bare film), i.e. the Purcell' effect.^[1, 2, 3] In the strong coupling regime instead excitons and photons lose their own identity creating a new mixed state called polariton.^[4] Strong coupling is currently under investigation for its role in quantum

electrodynamics and chemistry.^[2, 5, 6, 7, 8, 9] In spite of the complex physics of MCs, few simple concept can be easily understood. The defect between the DBRs (the cavity layer) breaks the periodicity of the multilayer stack and defines narrow, well-confined optical resonances that are highly sensitive to changes in the optical path length. As a consequence, the reflectance spectrum of the MC exhibits a minimum inside the wide reflectance peak due to the PBG, which represents a localized spectral window where light can couple into the cavity mode.^[10] The position, linewidth, and spatial confinement of these modes strongly depend on the thickness and refractive index of the defect layer, which can also be engineered to host active emitters in all the spectral ranges. The cavity-induced optical confinement can cause both a spectral redistribution of the oscillator strength and a modification of the radiative rate of the embedded material.^[11, 12, 13, 14]

Elastomeric microcavities are at the cutting edge of photonics, as mechanical deformation can change both the thickness and, occasionally, the refractive index of the layers involved, leading to variations in the PBG and cavity modes.^[15] This interaction between mechanical and optical properties opens up possibilities for adaptable photonic devices and the investigation of phenomena that depend on strain.^[16]

In this context, we designed and fabricated stretchable planar MCs based on multilayers of PFR94/SEBS-MAH, enclosing defect layers doped with emissive materials. Two different systems were investigated in detail: one incorporating the fluorescent polymer F8BT ((poly(9,9-dioctylfluorene-alt-benzothiadiazole))) and the other containing spiropyrans (SPs) molecules.

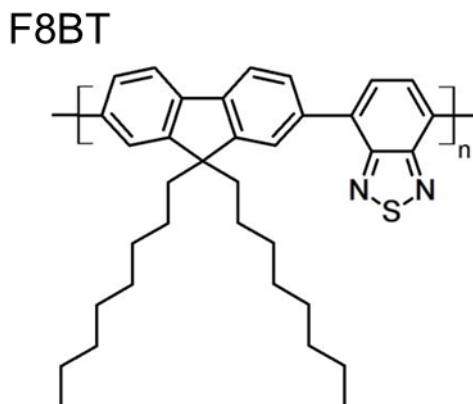


Figure 4.1: Molecular structure of F8BT

F8BT, also referred to as PFBT, is a fluorene copolymer extensively utilized in optoelectronic applications (Figure 4.1). It functions as a green-emitting polymer in organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic photovoltaic (OPV) devices. F8BT is notable for its high electron mobility, low energy level of the lowest unoccupied molecular orbital (LUMO), and stability in air, which makes it ideal for a range of electronic devices. Its distinct characteristics, such as deep HOMO and LUMO levels, enhance its effectiveness in energy conversion and luminous efficiency in OLEDs.

SPs are a class of molecular photoswitchers characterized by reversible isomerization between a closed, colorless spiropyran form and an open, colored merocyanine form (Figure 4.2). This transformation involves the cleavage of the C–O bond at the spiro center, leading to substantial changes in the physicochemical properties of the molecule, including its absorption spectra, dipole moments, and chemical reactivity.

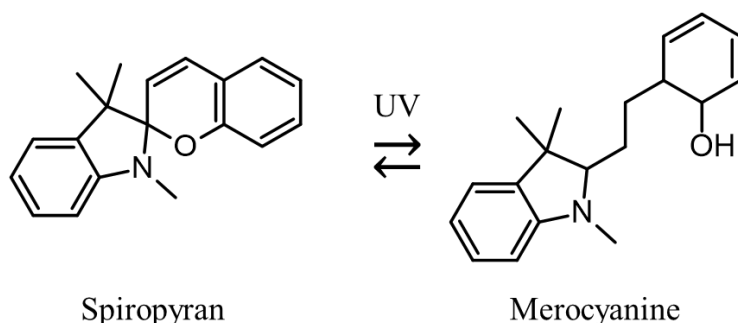


Figure 4.2: Isomerization of Spiropyran to Merocyanine.

Historically, SPs have been extensively investigated for their photochromic and thermochromic properties, with early studies dating back to the early 20th century.^[17] Over time, it has been recognized that this reversible ring-opening process can be triggered by a wide range of external stimuli, including light, temperature, pH, and mechanical force.

Mechanically induced SP-to-merocyanine conversion, an example of mechanochromism, has traditionally relied on the covalent attachment of SP molecules to polymer backbones. In such systems, the polymeric architecture and mechanical properties of the matrix play critical roles in force transduction to the SP molecule, promoting C–O bond cleavage under tension or compression. However, in the context of this PhD thesis we blended SPs molecules into a polymeric defect layer within a stretchable MC. This approach allowed us to investigate the mechanochromic response of SPs in a noncovalently constrained environment, demonstrating that the presence of a microcavity enhances and modulates their emission under applied strain. The microcavity provides a photonic environment in which SP emission can be spectrally sculpted, enabling continuous tunability of the mechanochromic response. While classical SP-containing polymers switch between two discrete color states, embedding SPs in an elastomeric microcavity enables a continuous and reversible spectral shift in response to mechanical deformation.

4.2. Materials and Methods

4.2.1. Sample Preparation

Microcavity with F8BT: The MC was fabricated on a glass substrate ($25 \times 25 \times 1 \text{ mm}^3$), which was first coated with a thick drop-cast layer of Chemiton (Franprene SRL) using 500 μL of a toluene solution (30 mg mL^{-1}). The MC was fabricated via dynamic spin coating, depositing

alternating layers of polymer solutions. Tecnoflon PFR94 (SYENSQO) was selected as the low-refractive-index component ($n \approx 1.32$) while the high-refractive-index material ($n \approx 1.5$) was a styrene-butylene-ethylene-styrene copolymer functionalized with maleic anhydride (SEBS-MAH). Specifically, Tecnoflon was dissolved in Galden HT 135 (Solvay Specialty Polymers S.p.A.) at a concentration of 60 mg mL^{-1} , while SEBS-MAH was dissolved in toluene at 30 mg mL^{-1} . $100 \text{ }\mu\text{L}$ of each polymer solution was sequentially deposited in alternating layers to build the final multilayer structure. Prior to each SEBS-MAH layer deposition, a low-pressure cold plasma treatment (Colibri-1B-MF, Gambetti Kenologia) was applied to the surface to enhance the wettability of the PFR layer, as described previously in Chapters 2 and 3.^[18] Tecnoflon PFR94 was used in its uncrosslinked form. The defect layer of the cavity was fabricated from a solution of F8BT (4 mg/mL) blended in a SEBS-MAH 60 mg/mL solution in toluene. The MC is composed of two multilayers composed of seven bilayers and a defect layer of up to a maximum of 29 layers. The complete scheme of the sample preparation is shown in Figure A1.3. The reference structure was prepared by depositing on top of a Chemiton thick supportive layer of three layers, resulting in a final structure PFR94-F8BT/SEBS-MAH-PFR94. The MC has been engineered in order to set the photonic band gap on the low energy side of the F8BT fluorescence spectrum.

Microcavity with SP: The MC was fabricated on a glass substrate ($25 \times 25 \times 1 \text{ mm}^3$), which was first coated with a thick drop-casted layer of Chemiton (Franprene SRL) using $500 \text{ }\mu\text{L}$ of a toluene solution (30 mg mL^{-1}). The MC was fabricated via dynamic spin coating, depositing alternating layers of polymer solutions. Tecnoflon PFR94 (SYENSQO) was selected as the low-refractive-index component ($n \approx 1.32$) while the high-refractive-index material ($n \approx 1.5$) was a styrene-butylene-ethylene-styrene copolymer functionalized with maleic anhydride (SEBS-MAH). Specifically, Tecnoflon was dissolved in Galden HT 135 (Solvay Specialty Polymers S.p.A.) at a concentration of 60 mg mL^{-1} (Solvay Specialty Polymers S.p.A.), while SEBS-MAH was dissolved in toluene at 30 mg mL^{-1} . $100 \text{ }\mu\text{L}$ of each polymer solution was sequentially deposited in alternating layers to build the final multilayer structure. Prior to each SEBS-MAH layer deposition, low-pressure cold plasma treatment (Zepto, Diener Electronic) was applied to the surface to enhance the wettability of the PFR layer, as described in the previous Chapters. Tecnoflon PFR94 was used in its uncrosslinked form. The defect layer of the cavity was fabricated from a solution of SP (2% wt/wt) blended in a SEBS-MAH 30 mg/mL solution in toluene. The MC was composed of two multilayers of 11.5 bilayers each and a defect layer for a total of 47 layers. The complete

scheme for sample preparation is shown in Figure A1.3. The reference structure was prepared by deposition on top of a Chemiton thick supportive layer of three layers, resulting in the final structure PFR94-SP/SEBS-MAH-PFR94.

4.2.2. Characterization

MC with F8BT: Reflectance spectra were obtained using a Y-probe optical fiber probe (FCR-7UVIR200, Avantes). A deuterium-halogen lamp (DH-2000-BAL, Ocean Optics) with a spectral range of 230–2500 nm was employed as the light source. The reflected signal was collected using an Avaspec-ULS2048CL-EVO-RS detector with a spectral range of 200–1100 nm and a resolution of 1.4 nm. An aluminum mirror served as the white reference spectrum. Angle-resolved transmission was assessed using a custom-built optical setup that included optical fibers (FG400AEA, diameter 400 μm , NA 0.22) coupled with a deuterium-halogen lamp (DH-2000-BAL) and a spectrometer (Avaspec-ULS2048CL-EVO-RS); the spectra were recorded at 5° intervals, ranging from 0° to 90°. Angle-resolved fluorescence was measured with a similar configuration, but the sample was irradiated with a continuous laser source, specifically a 405 nm CW laser from the MatchBox series, focused on a 1 mm diameter spot. Prior to the mechanical characterization, each DBR with its elastomeric support was meticulously detached from the glass substrate. The optomechanical characterization was conducted by integrating the optical fiber-based measurement system into a tensile testing machine (Instron 5565). Light from the Ocean Optics DH-2000-BAL source was delivered to the sample via an optical fiber, and the transmitted signal was collected and directed to a previously described UV–vis spectrometer. Simultaneously, the tensile machine recorded stress–strain curves of the samples. Fluorescence measurements were performed using the same setup, with a fiber laser at 405 nm as the light source and a 450 nm long pass filter (Thorlabs).

MC with SP: Normal-incidence reflectance spectra were obtained using a custom-designed optical fiber-based system. A light beam from a light source (AvaLight-CAL (-Mini) spectral range) was directed onto the DBR surface via a UV–vis–optical fiber probe (Avantes QP230-2-XSR). The resulting signal was transmitted to a UV–vis detector (Ocean Optics QEPro) for analysis. Prior to mechanical characterization, each DBR with elastomeric support was detached from the glass substrate. The optomechanical characterization of the samples was conducted using a custom-built optical fiber setup integrated into a tensile machine, focusing on rectangular samples with

dimensions of 20 mm $\times$ 5.5 mm $\times$ 0.05 mm (length $\times$ width $\times$ thickness). The experiments were performed on a Linkam TST350 microtensile stage equipped with a 20 N load cell at a strain rate of 100 $\mu\text{m s}^{-1}$, with a maximum strain value of 100%. Fluorescence spectra of the polymer films as a function of mechanical strain were recorded using an Ocean Optics QEPro spectrometer connected to an Ocean Optics LS-450 LED light source with an excitation wavelength of $\lambda_{\text{ex}} = 405$ nm and an optical fiber (Avantes FCR-7UVIR200-2-ME) employing a long-pass 450 nm filter for collection (Thorlabs). The complete schematic of the measurement set up is shown in Figure A3.5.

4.3. Results and Discussion

4.3.1. MC with F8BT

A schematic of the cavity structure, composed of two PFR94/SEBS-MAH DBRs enclosing a central defect layer of F8BT blended with SEBS-MAH, is shown in Figure 4.3a. Before detaching the microcavity (MC) from the rigid substrate used for fabrication, we performed preliminary measurements to evaluate one of the hallmark characteristics of the optical response of planar microcavities: their angular dependence on the incident light. In Figure 4.3b, we compare the normal-incidence transmittance spectrum (red curve) with the corresponding photoluminescence (PL) spectrum (black curve). The transmittance spectrum reveals the presence of a PBG centered between 600 and 750 nm, along with two cavity modes that appear as transmission maxima at 625 nm and 675 nm, highlighted in the plot with the use of two black arrows. The presence of multiple cavity modes was consistent with the relatively large thickness of the defect layer. The PL spectrum exhibits a broad and intense emission band between 500 nm and 750 nm, characteristic of F8BT. Notably, in correspondence with the two cavity modes observed in transmittance, the PL emission shows two clear local minima inside the main peak at 625 nm and 675 nm.

Figure 4.3c shows the stack plot of the MC emission spectra as a function of the increasing detection angle. As the detection angle increases, the emission spectrum gradually change its shape. The red dashed curve has been superimposed as a guide to the eye: making it easier to identify the angular positions at which the emission spectrum undergoes a clear modification due to spectral overlap with the two cavity modes. Figure 4.3d and Figure 4.3e shows, respectively, the stack plot of angle-resolved transmittance spectra for s-polarized and p-polarized light. In both cases, the photonic band gap is visible as a broad region of low transmission, within which the two

cavity modes appear as narrow high-transmittance branches. The red dashed lines matches the two cavity modes and are now used as a reference to better visualize how they shift as the incident angle increases. As expected for a multilayer cavity, both modes move progressively toward shorter wavelengths with increasing angle.

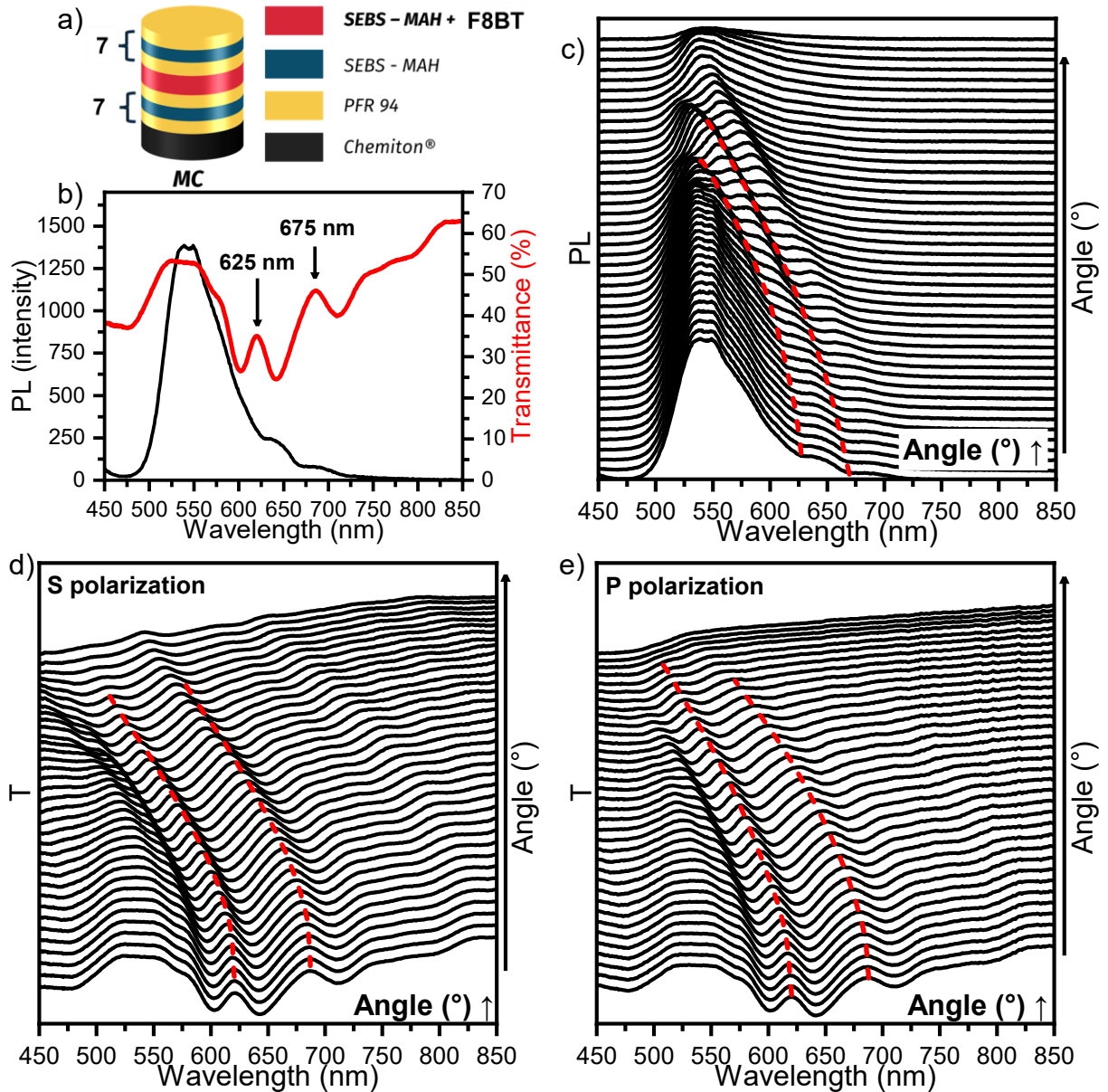


Figure 4.3: a) Schematic of the complete structure of the MC, b) PL (black curve) and transmittance (red curve) of the MC at normal incidence, c) stack plot of the PL (black curves) of the MC for different detection angles, d) and e): stack plot of the Transmittance of the MC for, respectively, S- and P-polarizations for different detection angles. The red dashed lines are useful to the reader for detecting the optical shift with the angle.

Having confirmed that this stretchable MC behaves as expected from theory, we proceeded to detach it from the rigid glass substrate to investigate its optomechanical response. We measured the transmittance and PL as a function of the applied strain, up to a maximum elongation of 100% in the elongation and contraction cycle. The results, shown in Figure 4.4a and b, are presented as contour plots, with the strain percentage on the y-axis (the elongation cycle displayed in the lower part of the color map and the contraction cycle in the upper part), the wavelength on the x-axis, and the transmission or PL intensity encoded in color for both elongation and relaxation cycles. In the transmission colormap, the PBG appears as an orange band against a violet background, while the two cavity modes are visible as violet features within the orange region, shifting in spectral position upon stretching. A black dashed line has been added at the location of the cavity modes as a guide to the reader, highlighting their position and making their strain-dependent shift easier to follow. At rest, the two cavity modes were located at 590 nm and 650 nm; at maximum elongation, they shifted to 440 nm and 480 nm, and upon relaxation, they returned to 600 nm and 640 nm. In the corresponding PL colormap, the F8BT emission appears as a ~50 nm wide orange band on a violet background positioned between 525 nm and 575 nm. A careful inspection revealed the progressive shift of the PBG and the two cavity modes across the emission peak, resulting in additional orange band appearing when the cavity modes are matching with the emission of F8BT. Here as well, the black dashed lines are drawn over the orange regions to highlight them for the reader, helping identify the spectral areas of overlap and clarifying how the PBG and the cavity modes shape the emission spectrum of F8BT. At ~450 nm we observe a orange band, which corresponds to the residual excitation light from the laser used in the measurements. Despite the use of a filter, the optical configuration of the setup did not allow for the complete suppression of laser excitation.

To verify that this strain-dependent PL modulation originated only from the cavity and not from the F8BT layer itself, the same measurements were performed on a reference sample lacking the cavity structure, consisting only of three layers, two layers of PFR94 surrounding the central cavity layer made of F8BT, fabricated under the same conditions used for the cavity structure. Figure 4.4c shows the optomechanical PL data for the reference sample, again shown as a colormap with strain on the y-axis (the elongation cycle in the bottom part and the contraction cycle in the upper part), wavelength on the x-axis and in color scale the emission. In this case, the F8BT emission appeared

as a stable orange band on a violet background with no additional features, remaining constant throughout the entire deformation cycle. We also monitored the mechanical response of the sample during optical measurements. Figure 4.4d shows the stress–strain curves for elongation (black curve) and relaxation (red curve). The sample exhibited elastic behavior up to approximately 15% strain, after which plastic deformation occurred. A small hysteresis between elongation and relaxation was observed, indicating that the sample retained its mechanical properties reasonably well over a full deformation cycle.

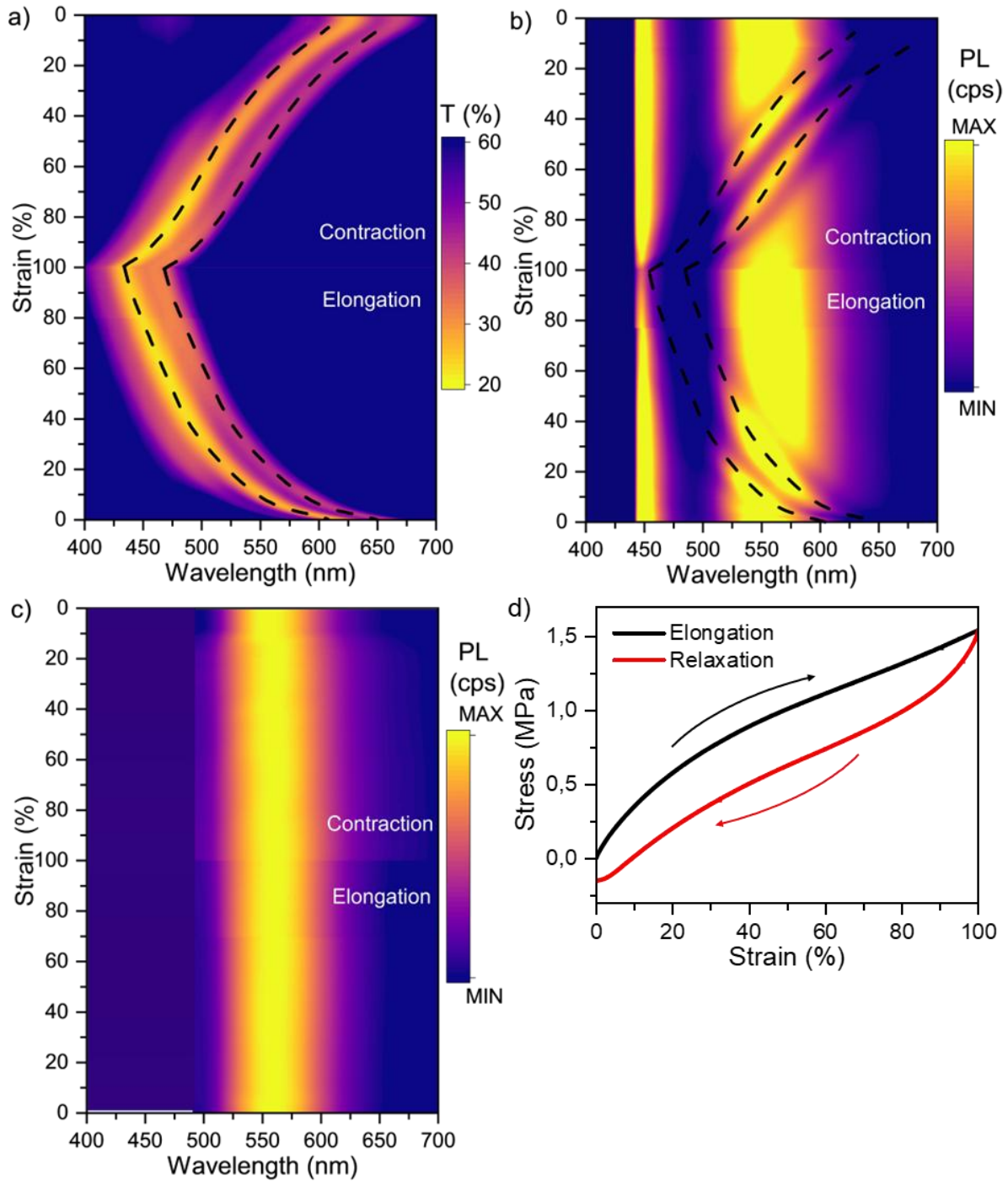


Figure 4.4: a) color map of the transmittance of the MC (color scale) at different values of strain for the elongation (bottom part) and contraction (upper part) cycles, b): color map of the PL of the MC (color scale) at different values of strain for the elongation (bottom part) and contraction (upper part) cycles, c): color map of the PL (color map) of the reference sample at different values of strain for the elongation (bottom part) and contraction (upper part) cycles, d): stress vs strain curve of the MC for the elongation (black curve) and relaxation (red curve) cycles.

The results obtained from the transmittance and PL measurements on both the MC and the reference are also summarized in Figure 4.5 in the form of stacked plots. Figure 4.5a, b and c, respectively reports the stack plot of the transmittance of the MC, PL of the MC and of the reference as a function of strain in the elongation (bottom part) and contraction (upper part) cycles. This visualization clearly shows the spectral shape of the transmittance and PL of MC and reference highlighting how the cavity modes modulate the F8BT emission when spectral overlap occurs. It is also evident how no mechano-optical effects are present in the reference, where the peak emission of the F8BT remains constant during the entire deformation cycle. In the PL spectra of the MC, we also observed the additional feature at about 450 nm already observed in the color maps, which, as previously mentioned, corresponds to the residual excitation light from the laser used in the measurements.

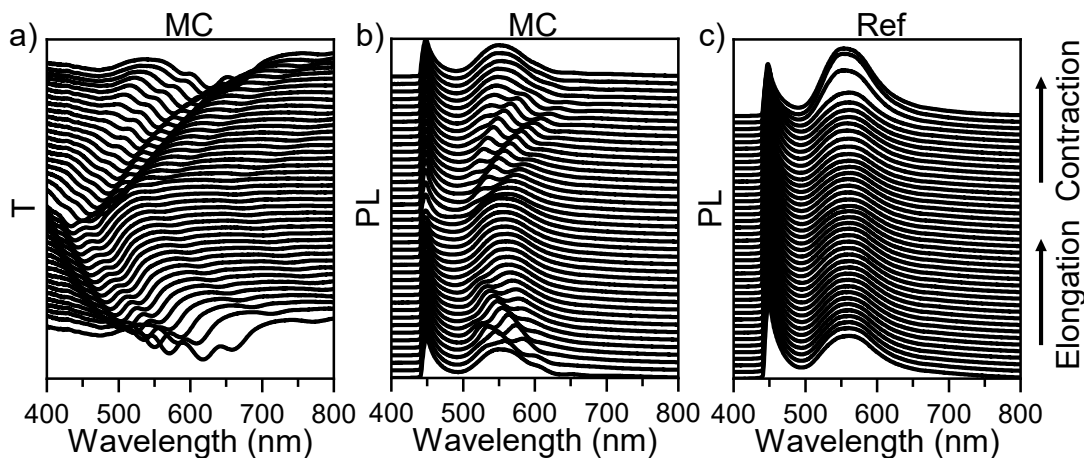


Figure 4.5: Stack plot of the optical response as a function of strain in the elongation (bottom part) and relaxation (upper part) cycles for a) transmittance of the MC, b) PL of the MC and c) PL of the reference sample.

4.3.2. Microcavity embedding a Spiropyran derivative

Unlike the first MC embedding the F8BT conjugated polymer, used primarily as a testbed to gain familiarity with the PL response in this class of elastomeric photonic nanostructures, the second MC, incorporating SP as the photo-active material, was conceived as an initial exploratory attempt to assess whether a stimuli-responsive photonic structuring could expand the functional behaviour of the embedded emitter. The results presented below should therefore be regarded as highly preliminary and with the awareness that additional experiments will be necessary to fully validate

the observations. Nevertheless, these early data suggest that the presence of the MC has the potential to transform the mechanochromic response of SP from a binary two-color behaviour, arising from the well-known spiropyran-to-merocyanine isomerization (Figure 4.2), into a continuously tunable spectral modulation. In Figure 4.6a, we present a schematic of the MC and the reference sample, alongside the molecular structure of the SP species incorporated into the defect layer. In this study, we primarily focused on the PL response, choosing an excitation wavelength of 405 nm in order to minimize the contribution of the intrinsic photoswitching between the spiropyran and merocyanine forms. By working at this wavelength, we deliberately aimed to bypass the photochemical conversion and to assume that the switching process had already occurred, allowing us to concentrate exclusively on the optical response of the system under mechanical deformation. For this reason, the photoswitch itself will not be further discussed in the following sections, as it remains one of the aspects requiring additional dedicated investigation. Figure 4.6b compares the PL spectra of the MC (red curve) and reference (grey curve). The MC spectrum exhibits a 100 nm-wide emission band containing three distinct peaks: one at 540 nm, a more intense peak at 585 nm, and a third at tot 625. In contrast, The reference spectrum did not exhibit any well-defined observable emission peaks, probably due to limitations of the measurement setup. In contrast, the emission from the cavity was significantly more intense. As already observed in Chapter 3, this enhancement may also arise from back-reflection effects induced by the presence of a DBR underneath the emitter, which amplifies the detected PL signal. These observations, however, should be considered preliminary, and further measurements will be required to confirm the origin of the enhanced emission. The reflectance spectrum revealed a PBG spanning 575–700 nm, with two minima located at 625 nm and 575 nm corresponding to a cavity mode, and to the PBG short wavelength edge, respectively. The main emission peak observed in the PL spectrum (at 585 nm) is expected to correspond to the cavity mode visible as a reflectance minimum in the reflection spectrum (at 625 nm). However, an unexpected spectral shift of approximately 50 nm appears between the two measurements. This discrepancy is likely related to intrinsic characteristics of the microcavity that have not yet been investigated.

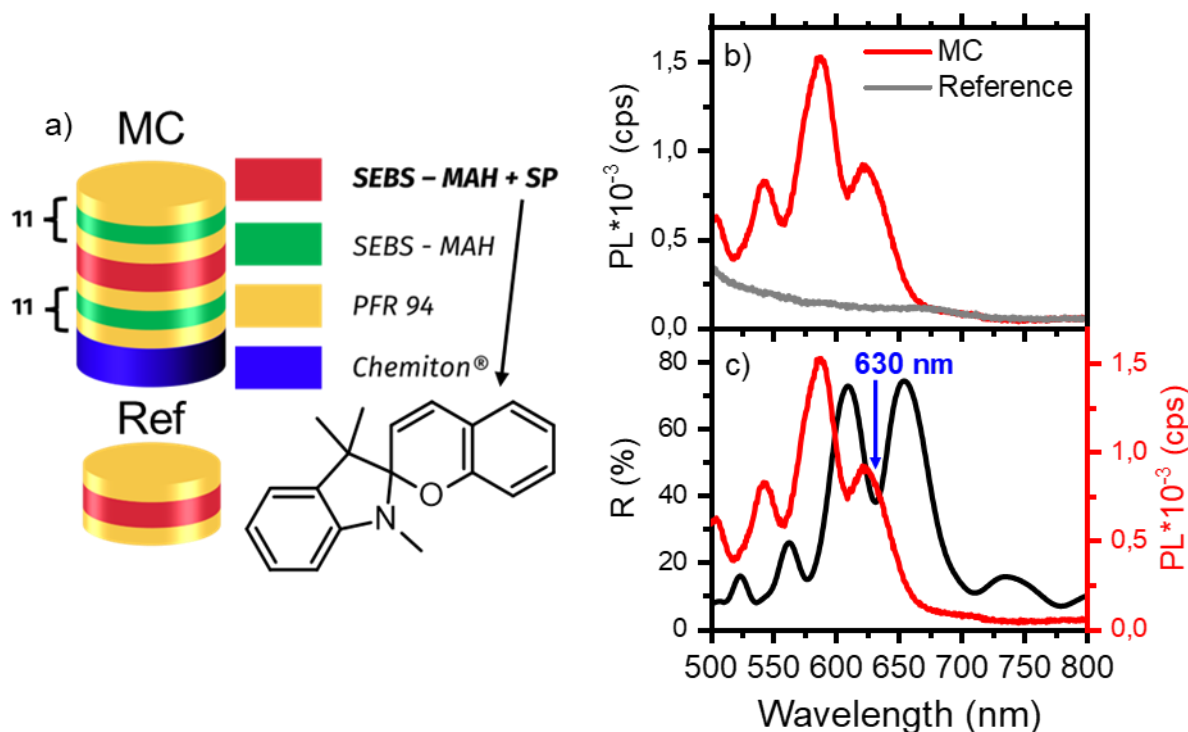


Figure 4.6: a) Schematics of the MC and Reference sample, b) PL spectra of the MC (red curve) and reference (grey curve) sample, c) Reflectance (black curve) and PL (red curve) of the MC.

We then detached the MC from the substrate and investigated its optomechanical response to 405 nm excitation. First, we collected the reflectance spectra as a function of the applied strain. The reflectance data are reported in Figure 4.7a as contour plot with strain (elongation and relaxation cycles) on the y-axis, wavelength on the x-axis and normalized reflectance in color scale. The reflectance colormap displays the PBG as a wide violet band, while the cavity and edge modes are shown as reddish bands. A white dashed line has been included as a visual guide to assist the reader in identifying the cavity mode. In its resting state, the central cavity mode and the lateral edge were positioned at respectively 640 nm and 590 nm. When strained, the lower energy one shifted to 500 nm at maximum elongation, the other cavity mode is no more detectable because it is positioned outside the filter range. Both spectral features return to 550 and 600 nm, respectively, once the sample is fully relaxed. In Figure 4.7b, we also included a stack plot showing the reflection spectra recorded at every 10% strain increment. The red dashed line serves again as a visual guide,

allowing the reader to follow the shift of the cavity mode throughout both the elongation and relaxation cycles.

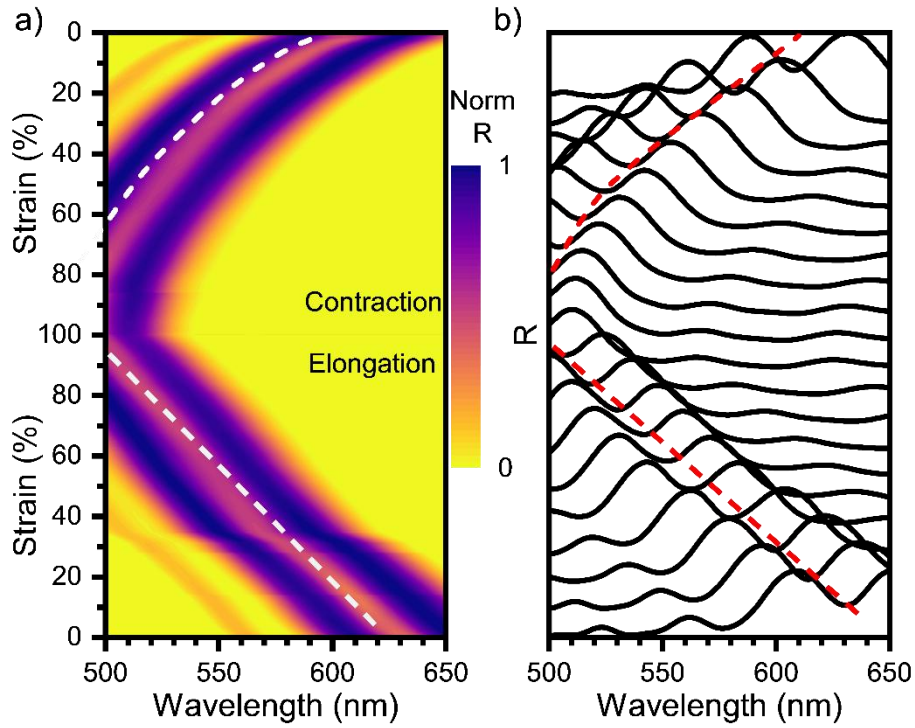


Figure 4.7: a) Color map of the Normalized Reflectance (color scale) as a function of the strain in the elongation (bottom part) and relaxation cycles (top part), b) stack plot of the reflectance spectra collected each 10% of strain.

We then focused on the strain-dependent PL response of the cavities. Figure 4.8a shows the corresponding PL contour plots, with strain on the y-axis, wavelength on the x-axis, and normalized PL intensity in the color scale. During both the elongation (bottom part) and relaxation (upper part) cycles, the PL appears as a ~ 100 nm wide violet band on a yellowish background with two distinct peaks: a stronger one centered at 585 nm and a weaker one at 620 nm. These features correspond again cavity mode and to the lateral edge, respectively.

For clarity, in Figure 4.8b compare the normalized PL spectra (red curve) and normalized reflectance spectra (black curve) of the MC at strain intervals of 20%. This representation is intended exclusively to highlight the strain-dependent shift of both spectra. To verify whether the newly observed shift in the emission could indeed arise from the microcavity rather than from the SP layer itself, we repeated the optomechanical PL measurement on the reference sample. Figure

4.8c presents the results as a colormap with the strain on the y-axis, wavelength on the x-axis, and PL intensity on the color scale. In this case, the PL appeared as a violet band on a light orange background with no strain-induced modulation throughout the elongation–relaxation cycle. These results may indicate that the cavity could endow the SP with a new form of mechanochromic behaviour featuring a degree of spectral continuity. Instead of exhibiting only the typical two-state response associated with its conformational switching, the emission appears to shift continuously across the ~650–600 nm range under applied strain. However, this should be regarded only as a preliminary indication, and further investigations will be required to confirm and fully understand this behaviour. The correlation between the emission peak wavelength (indicated by stars in the graphs) and strain during elongation (red curve) and relaxation (black curve) is shown in Figure 4.8d. The near overlap of the two traces demonstrates that the mechanochromic response exhibits no hysteresis and is highly reversible.

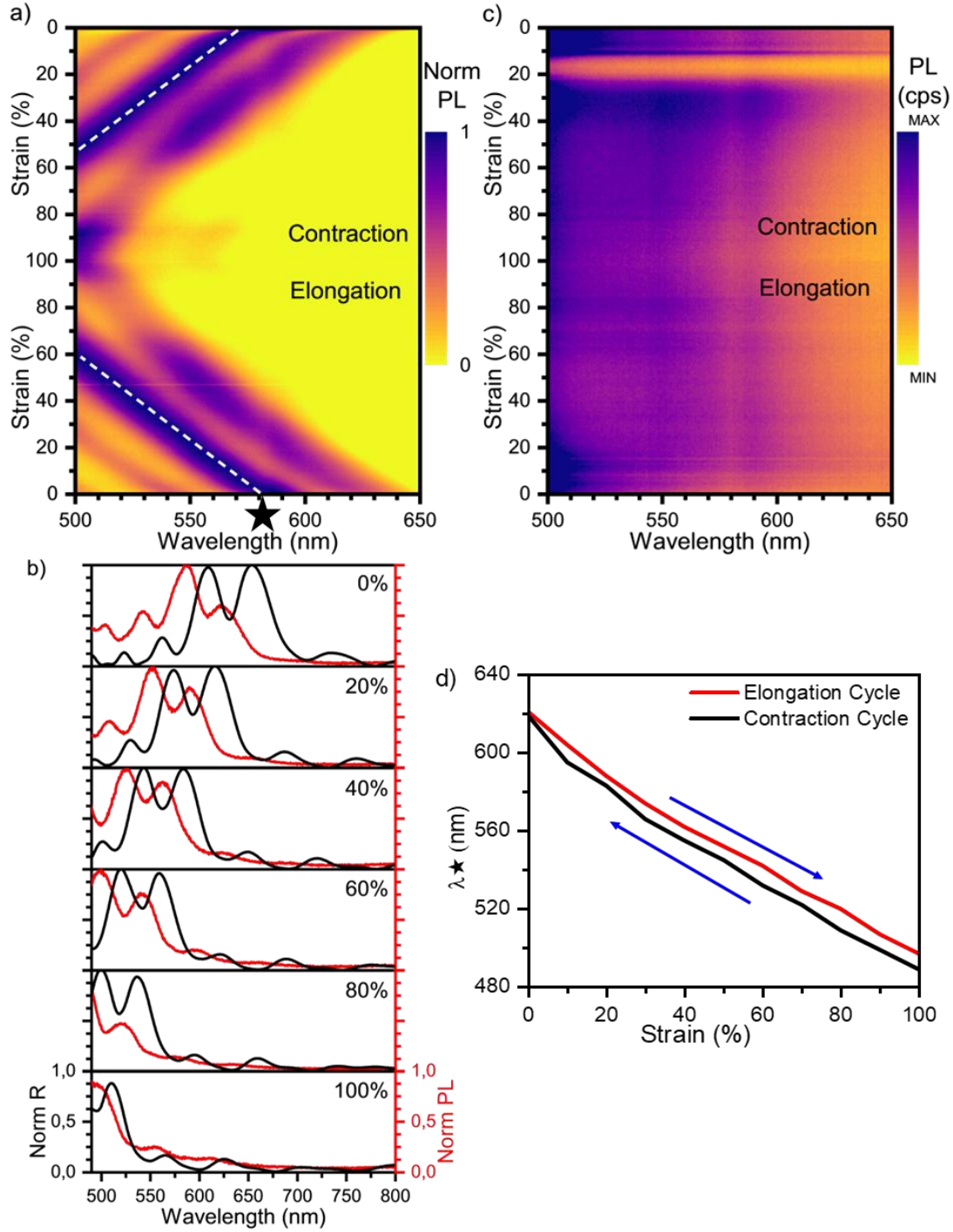


Figure 4.8: a) Contour plot of the PL of the MC (color scale) as a function of the strain in elongation (bottom part) and relaxation (top part) cycles; b) Reflectance (black curve) and PL (red curve) at 0%-20%-40%-60%-80%-100% values of strain; c) Contour plot of the PL of the reference sample (color scale) as a function of the strain in elongation (bottom part) and relaxation (top part) cycles; d) wavelength of the star peak in the PL contour plot as a function of the strain in the elongation (red curve) and contraction cycle (black curve).

4.4. Conclusions

In this chapter, we have shown how planar polymer-based microcavities (MCs) can be designed, fabricated, and exploited to achieve mechano-responsive photonic functionalities. Starting from the fundamental principles of planar MCs, active emitters were integrated into elastomeric architectures and their optical responses investigated under both angular variation and mechanical deformation. The first system, based on F8BT, provided a benchmark for verifying the optomechanical behavior of the stretchable MC platform. Angular-resolved measurements confirmed the presence of photonic bandgaps and cavity modes, while strain-dependent experiments revealed a reversible modulation of both transmittance and photoluminescence (PL). Comparative measurements with a reference sample demonstrated that the observed mechano-responsivity originated from the cavity structure, highlighting the critical role of the photonic environment in shaping the emission of the embedded material. Building on this foundation, a second system incorporating spiropyran (SP), a mechanochromic molecule typically exhibiting binary color switching, was investigated. Preliminary results suggest that embedding SP within the MC enhances its mechanochromic response, enabling a continuous and reversible spectral tunability across tens of nanometers. Strain-dependent measurements suggest that photonic structuring can access mechanochromic regimes not achievable by isolated molecules alone. However, these observations are highly preliminary, and further experiments will be required to rigorously confirm the mechanisms and reproducibility of the SP-based systems.

Overall, these studies underscore the potential of stretchable planar MCs as versatile platforms for both fundamental investigations and technological applications. By combining mechanical flexibility with strong optical confinement, these architectures offer opportunities for the development of reconfigurable photonic devices, tunable light sources, and mechanochromic materials with functionalities beyond those of their constituent components. The integration of active materials into stretchable MCs opens the path toward a new class of mechanically reconfigurable photonic systems, though the exploration of SP-based mechanochromism will require additional systematic studies to fully establish its performance and reliability.

4.5. References

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5. Creating All-Polymer Multilayer Photonic Crystals Using Dip Coating Trough 3D Printer Modification

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Chapter at a Glance: Chapter 5 presents a side project in which a commercial FDM 3D printer was successfully adapted into a dip-coating system capable of producing polymer-based photonic structures, including distributed Bragg reflectors (DBRs) and planar microcavities. Two polymers, Aquivion and poly(N-vinylcarbazole), with low and high refractive indices respectively, were employed for DBR fabrication. The process was shown to be highly sensitive to parameters such as solution viscosity, withdrawal speed, drying conditions, and substrate characteristics. Initial optimization focused on withdrawal speed and drying conditions to enhance the formation of one-dimensional photonic crystals. To demonstrate the system's capabilities, a delicate planar microcavity was fabricated, partially using recycled materials, and its optical properties were characterized. Angle-resolved transmission and photoluminescence measurements confirmed that the photonic structure closely resembled spin-coated samples, with the expected shift of the photonic bandgap and cavity mode to shorter wavelengths at increasing collection angles. While this work represents a personal exploration rather than the core focus of the thesis, it provides valuable insights into the complexities of dip-coating for all-polymer photonic structures and establishes a foundation for potential further research and refinement in fabrication strategies.

5.1. Introduction

As a side project, I co-supervised Coralie Hervieu, a student from Sigma-Clermont University, who joined our lab as an Erasmus trainee to complete her internship project. The objective was to transform a commercial 3D printer into a dip-coater for creating all-polymer photonic multilayers, distributed Bragg reflectors, and planar microcavities (Figure 5.1).

Dip coating is a widely used technique for creating thin films. The process involves submerging a substrate into a casting solution with a known concentration. As the substrate is carefully withdrawn from the solution, a thin liquid film forms from the meniscus, and the solvent's evaporation results in the final film. The film's thickness is influenced by the initial solution's concentration, the speed of withdrawal, and the solvent's evaporation rate, which can be affected

by environmental conditions. Typically, dip-coating machines are quite costly and not ideal for producing DBRs, as they are limited to uniaxial movement, allowing them to dip into only one solution at a time, requiring manual changes by an operator to create alternating layers.^[1, 2]

In contrast, a 3D printer inherently supports triaxial movement, allowing it to move between two or more solutions and alternately dip into each of them. To adapt the printer for this purpose, we replaced the extruder head with a clip designed to hold glass substrates, which was crafted and 3D printed in acrylate resin. However, the printer requires a file containing a sequence of coded instructions to perform these operations. To produce a DBR, the head must descend to dip into the first solution, rise at a controlled speed, pause to allow the film to dry, and then move to the second solution. Repeating these steps completes the deposition cycle. To enable this process, a MATLAB script was developed by my colleague, Dr. Andrea Lanfranchi, to automatically generate the corresponding G-code from simple input parameters such as drying time, withdrawal speed, and solution levels.

To illustrate the practicality and effectiveness of the method, we present the creation of various polymer multilayers composed of poly(N-vinylcarbazole) (PVK, with a high refractive index of $n = 1.68$)^[3] and Aquivion (AQ, featuring a low refractive index of $n = 1.34$), a perfluorinated ionomer material.^[3] For the microcavity defect layer, a fluorescent material was derived from a polystyrene derivative sourced from a recycled ice cream spoon. It should be noted that, unlike in the previous chapters, detailed experimental procedures are not provided here, as this work represents a side project in which I actively co-participated but I didn't performed the experiments independently.

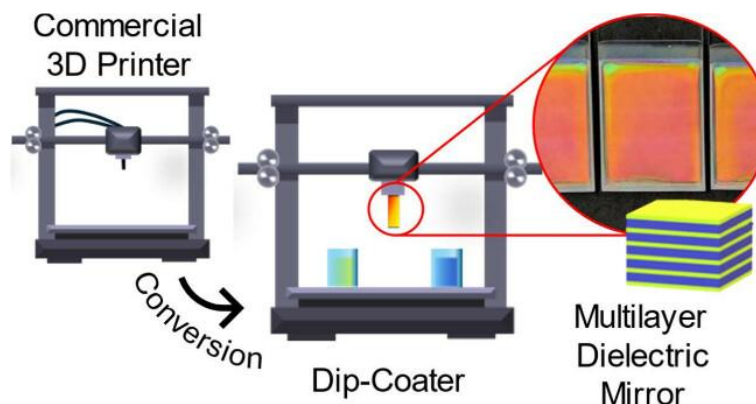


Figure 5.1: Scheme of the 3D printer conversion.

5.2. Results and Discussion.

DBR Fabrication: Initially, we created three samples consisting of 5.5 bilayers, each using different withdrawal speeds (1, 2, 4 mm s⁻¹) without applying any heat. Figure 5.2a illustrates the reflectance spectra taken from six distinct points on the surface of the multilayer produced at a withdrawal rate of 1 mm s⁻¹. In this particular sample, identifying features indicative of a photonic structure is not possible. Nevertheless, all spectra exhibit an interference pattern, visible as oscillations in the reflectance spectrum background, indicating a certain level of optical quality in the overall film. The slight rise in the background value towards the shorter wavelength region is attributed to the increasing refractive index of the PVK.^[3] The absence of distinct peaks in the reflectance spectrum is further evidenced by the digital image of the sample (inset), which displays an opaque bluish hue. When the withdrawal speed is increased to 2 mm s⁻¹ (Figure 5.2b), the optical quality of the sample improves, particularly in the upper section. Indeed, the spectra recorded at positions 2 and 3 reveal a photon bandgap centered at 448 nm with reflectance exceeding 60%. However, the sample remains largely inhomogeneous, with the rest of the surface showing light scattering features, which are also easily visible in the digital image of the sample. Finally, in the sample cast at a speed of 4 mm s⁻¹ (Figure 5.2c), all spectra display well-defined high reflectance peaks attributed to the photonic bandgap. This outcome confirms the formation of the dielectric lattice. However, these peaks are spread over a broad spectral range (from 470 nm to 800 nm), indicating the challenge of casting films with uniform thickness under these conditions. The wavelength of the photon bandgap is directly proportional to the layer thickness, suggesting variation across the sample's surface.^[4] This inhomogeneity is also clearly visible in

the digital photograph of the sample, which shows vivid and brilliant color transitions from blue to red as one moves from position 6 to position 1.

Data discussed so far also indicate that the thickness of the film increases as the withdrawal speed rises. Specifically, at higher speeds, the photonic bandgap is observed in the visible and near-infrared spectral ranges, whereas at lower speeds, it shifts toward the blue spectral region and becomes undetectable at the slowest withdrawal rates. According to dip coating theory^[1, 2], various forces come into play during the withdrawal phase. These forces are categorized into draining forces, which draw the liquid away from the substrate and back into the bath, opposing film deposition, and entraining forces, which retain the fluid on the substrate, promoting film formation. The balance between these forces determines two distinct regimes: one where thickness decreases with increased withdrawal speed when capillary entraining forces prevail, and another where thickness increases when draining forces are dominant. ^[5] The theory thus implies that the setup operates in the draining regime, a conclusion supported by the findings of Rauh et al. for similar withdrawal speeds.^[6] Variations in layer thickness can instead be attributed to the accumulation of solutions during the slow drying process.

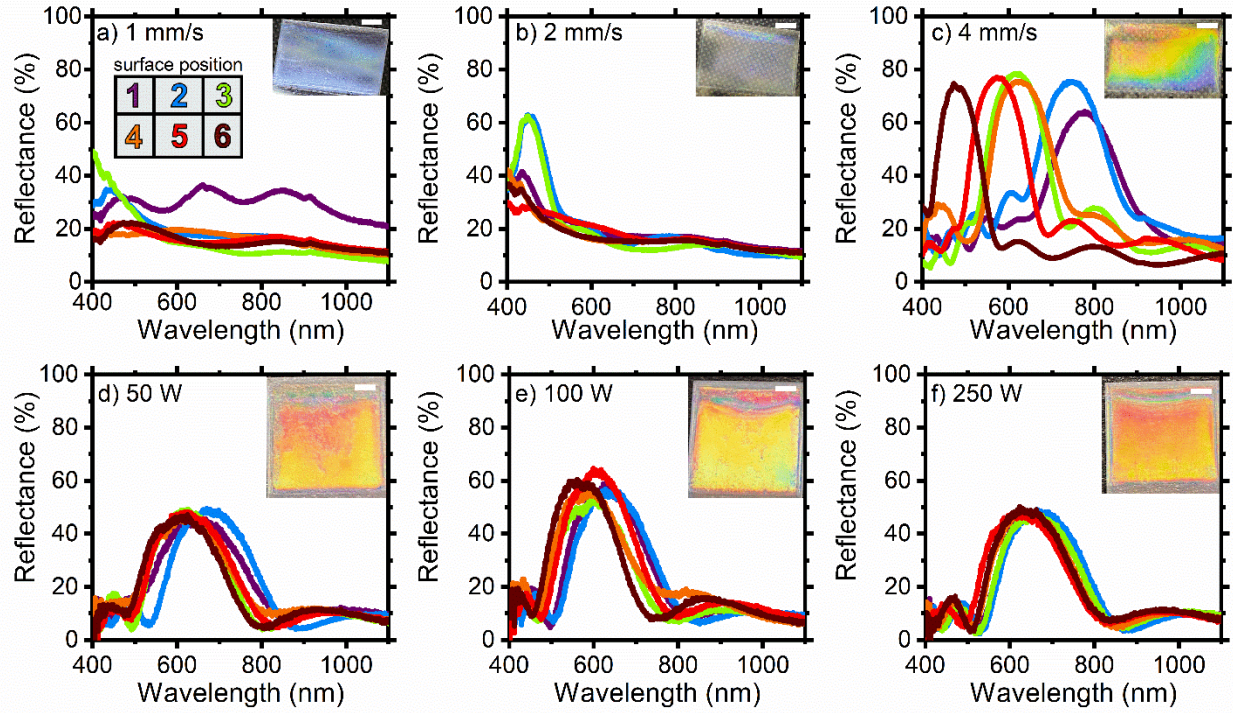


Figure 5.2: Reflectance spectra of the multilayers fabricated at withdrawal speed of (a) 1 mm s^{-1} , (b) 2 mm s^{-1} and (c) 4 mm s^{-1} and of samples fabricated at a withdrawal speed of 4 mm s^{-1} under infrared irradiation (d) 50 W, (e) 100 W, and (f) 250 W. The white line is 5 mm.

To accelerate the drying process, an infrared light source was employed to heat the sample during withdrawal. We experimented with three different infrared lamp powers (50-100-250 W) while keeping a constant withdrawal speed of 4 mm s^{-1} and using 3.5 bilayers. Starting with the lowest power setting of 50 W (Figure 5.2d), a distinct photonic band gap was observed between 605 nm and 675 nm. Despite some inhomogeneities, the spectra collected from various points on the sample showed good overlap. This is corroborated by the digital image in the inset, which reveals two primary color regions, indicating that while homogeneity has improved, it remains unsatisfactory. Consequently, the power was increased to 100 W (Figure 5.2e). The optical response of this new sample displayed a photonic band gap ranging from 564 nm to 633 nm. Although the increased lamp power did not seem to affect homogeneity, the intensity of the photonic band gap reflectance peak was higher than in the previous case. This led us to further increase the lamp power to 250 W (Figure 5.2f). Spectra collected from six points on the sample revealed a photonic band gap between 628 nm and 662 nm, with a spectral shift of approximately

30 nm. This sample was the most homogeneous, suggesting that higher lamp power optimizes drying conditions. The digital image shows a sample with a predominantly reddish uniform color, interrupted only by a yellowish shade at the bottom.

Microcavity Fabrication: To further evaluate the quality of the deposition systems beyond mere color uniformity, we constructed and analyzed a microcavity structure. The characteristics of this structure are highly dependent on the quality and consistency of the films used, such as uniform layer thickness and minimal interface roughness.^[7] To showcase the system's effectiveness even with suboptimal materials, the microcavity's fluorescent layer was crafted from a recycled ice-cream spoon. Under normal lighting, the spoon appears green, but it emits a bright cyan fluorescence when exposed to violet light. The composition of the spoon was confirmed using infrared spectroscopy, and its spectrum is displayed in Figure 5.3 alongside that of polystyrene.

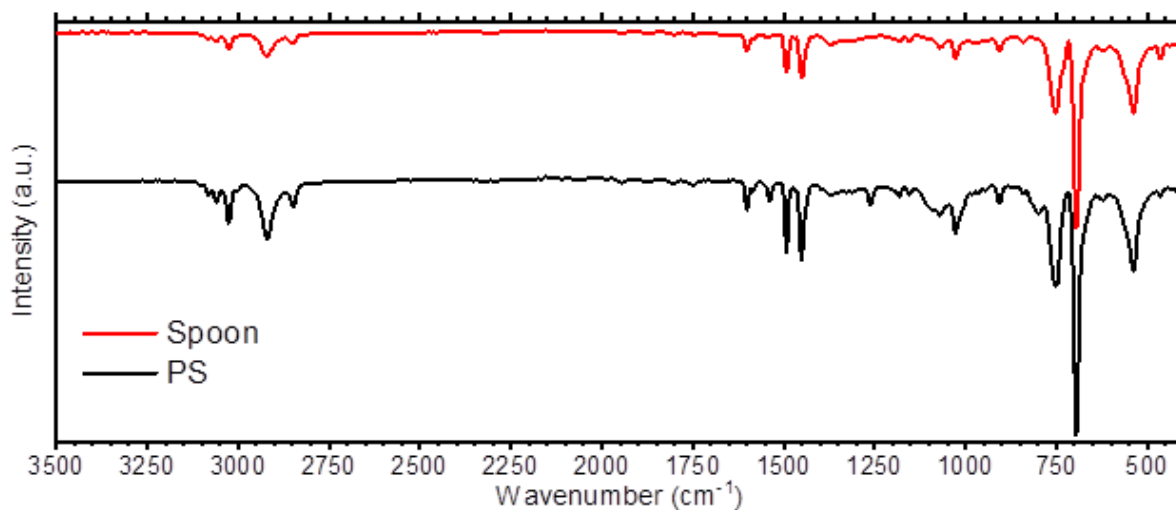


Figure 5.3: IR spectra of the drop cast cavity film (red) and reference polystyrene (black).

The sample displays aliphatic and aromatic C-H stretching peaks at 2924 and 2851 cm^{-1} , and at 3026 and 3082 cm^{-1} , respectively. Aromatic C=C stretching vibrations are noted around 1605 and 1585 cm^{-1} . In the 1490-1450 cm^{-1} range, two distinct peaks are associated with the bending vibrations of aromatic C-H bonds, which are characteristic signals of polystyrene. The exact composition of the xanthenic dye is unknown, and it is unclear whether it is dispersed or bonded

to the matrix; however, it is presumed to be fluorescein or a similar compound due to its color, affordability, and compatibility with food. A thorough investigation to confirm this is beyond the scope of this dissertation. The microcavity was created using two DBRs (PVK-AQ)⁵, as illustrated in Figure 5.4a, with the PS-dye defect layer sandwiched in the middle. The microcavity exhibits a vivid green color, visible in its digital image (inset of Figure 5.4b), with slight inhomogeneities at the edges where the glass substrate's border affects film deposition. In Figure 5.4b, the transmittance of the microcavity is shown as a black line, revealing a photon bandgap as a broad low-transmittance area between 400 and 600 nm. Within this bandgap, two relative transmittance peaks at 470 and 550 nm are observed, likely due to two cavity modes.^[7] The microcavity structure significantly alters the density of local photonic states in the system, thereby affecting the layer's emission. This, in turn, has a pronounced impact on the dye's fluorescence spectrum.^[8] To illustrate this effect, Figure 4b presents the fluorescence spectrum of a thin film of the PS-dye blend, cast under the same conditions used for the cavity, as a dotted green line. The spectrum is broad and intense, peaking asymmetrically at 480 nm. Conversely, the microcavity, consistent with theoretical predictions^[9], exhibits a significant spectral redistribution of its fluorescence (red line in Figure 5.4). Specifically, the signal is nearly entirely suppressed within the photon bandgap, while it is enhanced at the cavity modes compared to the dye film alone.

The influence of the photonic band structure on the optical spectra of the microcavity, including both transmittance and fluorescence, is further validated through angle-resolved measurements.^[10] Figure 5.4c and Figure 5.4d present the data sets as contour plots. The y-axis displays the collection angle for photoluminescence (4c) and transmittance (4d) in relation to the wavelength on the x-axis. Each angle-wavelength pair's transmittance and photoluminescence values are depicted as color gradients, with lighter yellowish tones indicating stronger emission and transmittance. In Figure 5.4d, the photonic bandgap (the dark blue, low-transmittance area) and the cavity mode (indicated by the dotted line) shift to shorter wavelengths as the angle of incidence increases. This blueshift is typical for photonic structures like DBRs and MCs, as documented in numerous studies.^[7, 11] The trend of the cavity mode, marked by the dashed black line, is closely paralleled by the change in the MC's photoluminescence with increasing angle. Indeed, the photoluminescence peak (the bright yellow band in Figure 5.4c, highlighted by the black dashed line) undergoes the same blueshift.^[7, 11] This behavior further confirms that the MC redistributes emission based on the spectral position of its cavity modes, enhancing the signal at these positions

and suppressing it at the photon bandgap. Additionally, around 35° , when the longer wavelength cavity mode aligns with the dye photoluminescence spectrum, the emission correspondingly increases. Overall, these measurements suggest that the structure functions as expected for a typical polymer MC.

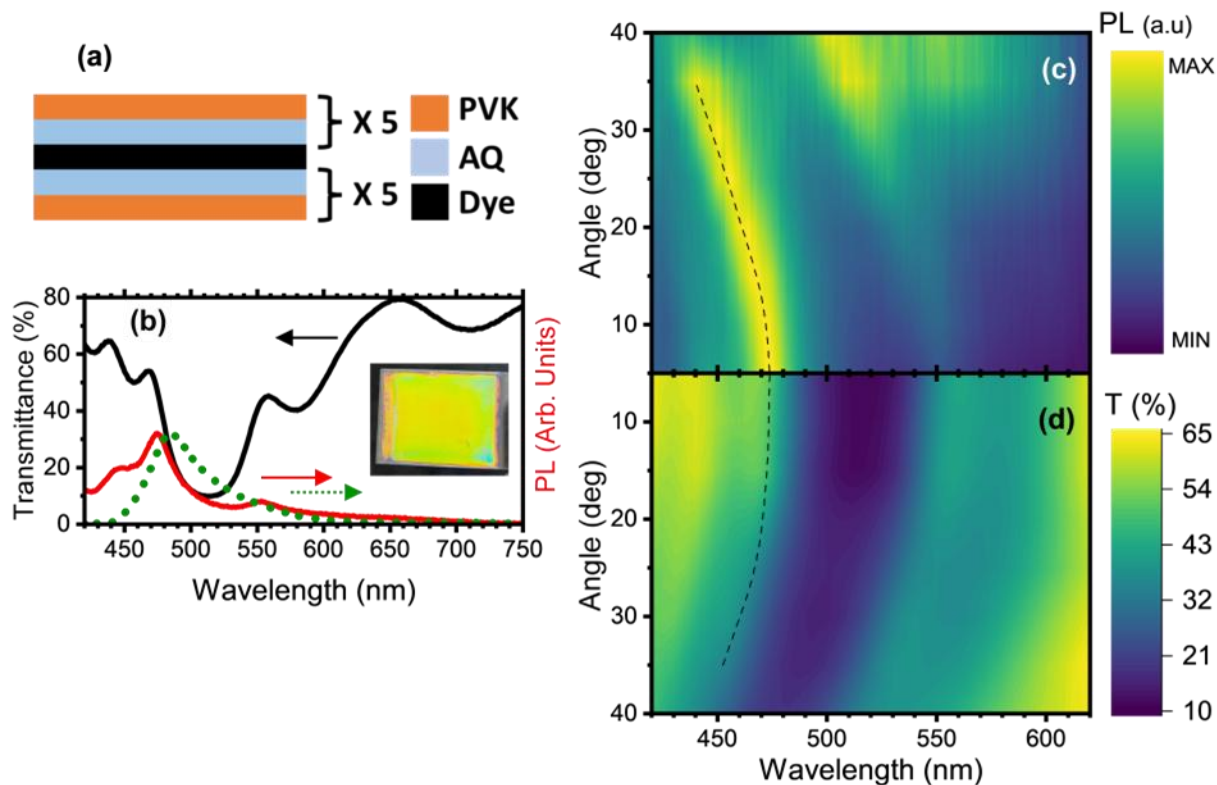


Figure 5.4: Figure 4: a) Schematic of the microcavity. b) Transmittance (black line) and PL (red line) spectra of the microcavity compared with the PL spectrum of a dye thin film (dotted green line). The inset shows a digital picture of the sample. c) and d) Angle resolved PL (c) and transmittance spectra (d) of the microcavity sample. The dotted line follows a cavity mode as a guide for the eye.

As illustrated in Figure 5.5, we conducted measurements of the radiative rate within the microcavity. We noticed a variation in the radiative rate due to changes in the dielectric environment compared to air. Overall, the findings related to microcavity fabrication, aside from minor effects on the radiative rate, demonstrate that the dip-coating microcavity growth process achieves the precision necessary for producing optical quality microcavities.

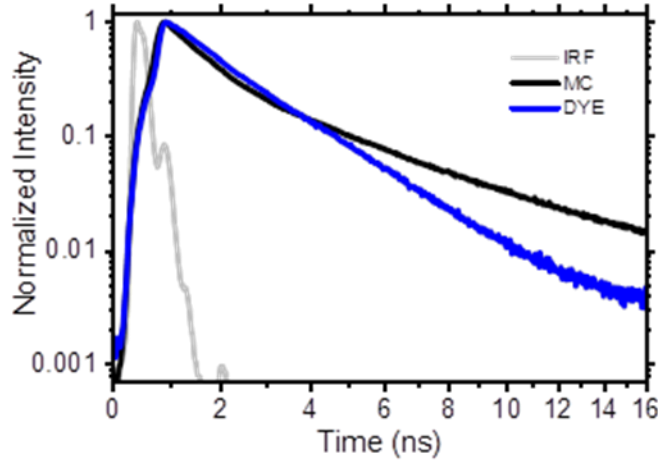


Figure 5.5: Comparison of the fluorescence decay upon excitation with a pulsed laser ($\lambda=405\text{nm}$) for the standalone defect film (blue), MC (black), and the IRF (gray) in a log-log plot.

5.3. Conclusions

This chapter clearly illustrates the effective transformation of a commercial FDM 3D printer into a dip-coating system capable of producing photonic structures like DBRs and planar microcavities. Two polymers, Aquivion and poly(N-vinylcarbazole), with low and high refractive indices respectively, were employed as materials for constructing DBRs. The dip-coating process is influenced by a careful balance of factors, including solution viscosity, withdrawal speed, drying conditions, and substrate characteristics. As an initial investigation, withdrawal speed and drying conditions were optimized to enhance the fabrication of one-dimensional photonic crystals. To test the system's capabilities, a delicate photonic structure, the planar microcavity, was created, partially using recycled materials. Its optical characterization revealed the typical features documented in literature for this type of microcavity, as well as their influence on the photoluminescence of the embedded dye. The resemblance of the microcavity's photonic structure to that of spin-coated samples is further corroborated by angle-resolved transmission and photoluminescence measurements, which demonstrate the usual shift of the photon bandgap and microcavity mode to shorter wavelengths as the collection angle increases. We believe the findings from this experimental approach illuminate the complex aspects of the dip-coating process for all-polymer photonic structures and will provide a foundation for further research and refinement in this area.

5.4. References

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6. Conclusions

This thesis has provided a broad exploration of polymer-based mechanoresponsive photonic systems, highlighting the interplay between material design, fabrication strategies, and optical functionality. The core studies demonstrate that thermoplastic perfluorinated polymers combined with styrene-based block copolymers can be effectively employed to construct distributed Bragg reflectors (DBRs) with tunable mechanical and optical properties (Chapter 2). The transition from a first to a second generation of stretchable DBRs, enabled by dynamic spin-coating and the use of alternative styrene-based thermoplastics, brought clear improvements in optical quality and mechanical performance, while also allowing the creation of free-standing, substrate-free structures that serve as platforms for further investigation. These results underscore the potential of carefully engineered polymer architectures to provide versatile and resilient photonic systems.

The integration of supramolecular mechanophores, such as Loop-HMDI-PU, into these DBRs further illustrates how molecular-scale mechanochromic motifs can be coupled with photonic structures to achieve controlled and reversible modulation of emission (Chapter 3). The interplay between mechanophore emission and photonic multilayers opens exciting avenues for multifunctional devices, from tunable light sources to responsive coatings, without the need for chemical modifications.

Planar microcavities (MCs) embedded with active emitters offered another dimension to these investigations (Chapter 4). Here, photonic structuring enabled the enhancement of mechanochromic responses, as seen with spiropyran (SP), extending its traditional binary switching to a continuous and reversible spectral tunability. While these findings are promising, they remain highly preliminary, and additional systematic studies will be necessary to confirm the reproducibility, mechanisms, and long-term behavior of SP-based systems.

Alongside these main studies, a side project explored the adaptation of a commercial FDM 3D printer into a dip-coating system for fabricating photonic structures (Chapter 5). Although this work provided valuable insights into fabrication parameters and hands-on experience, it was pursued independently and does not constitute the core of the thesis.

Overall, this thesis demonstrates the versatility of stretchable polymer-based photonic architectures as platforms for both fundamental studies and technological applications. By combining mechanical flexibility with strong optical confinement, these systems allow the realization of reconfigurable photonic devices and mechanochromic materials with enhanced functionalities. While the detailed conclusions and experimental analyses are presented within each chapter, the collective outcome highlights a pathway toward mechanically reconfigurable photonic architectures that bridge molecular phenomena and macroscopic device performance, laying the groundwork for future explorations in optomechanical sensing and adaptive photonic technologies.

Appendices

Appendix 1: Supplementary Figures for Materials and Methods

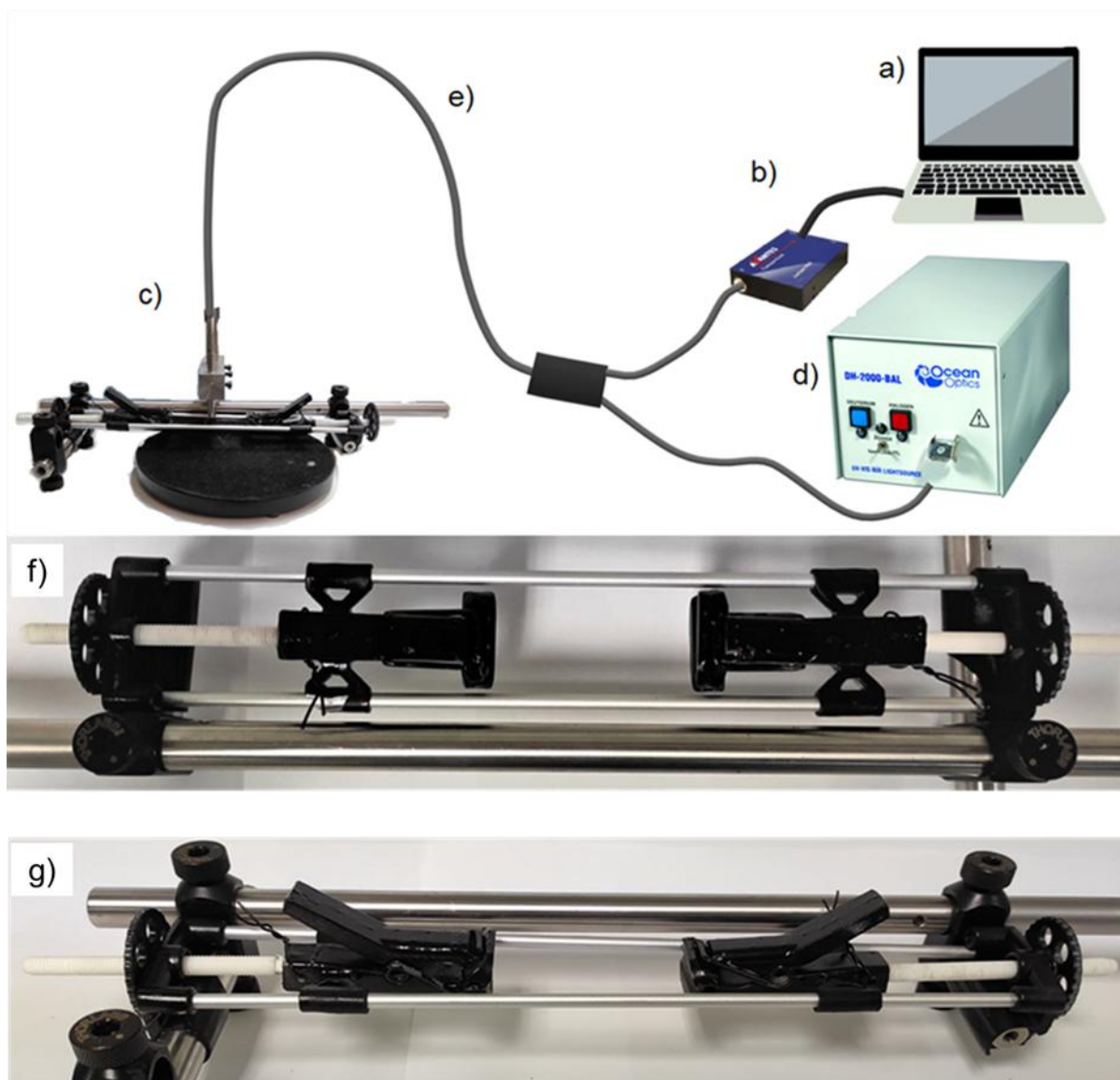


Figure A1.1: Schematic of the custom-built optical fiber-based setup integrated with a 3D-printed tensile device used for the optical-mechanical reflectance measurements, and top and side views of the 3D-printed tensile device. The entire system consists of analysis software (a), a UV-VIS spectrometer (b), a 3D-printed tensile device (c), a deuterium-tungsten halogen light source (d), and a UV-vis-NIR optical fiber (e). The tensile device (f, g) allows samples to be stretched by clamps connected to a metric screw that can be controlled by a gear.

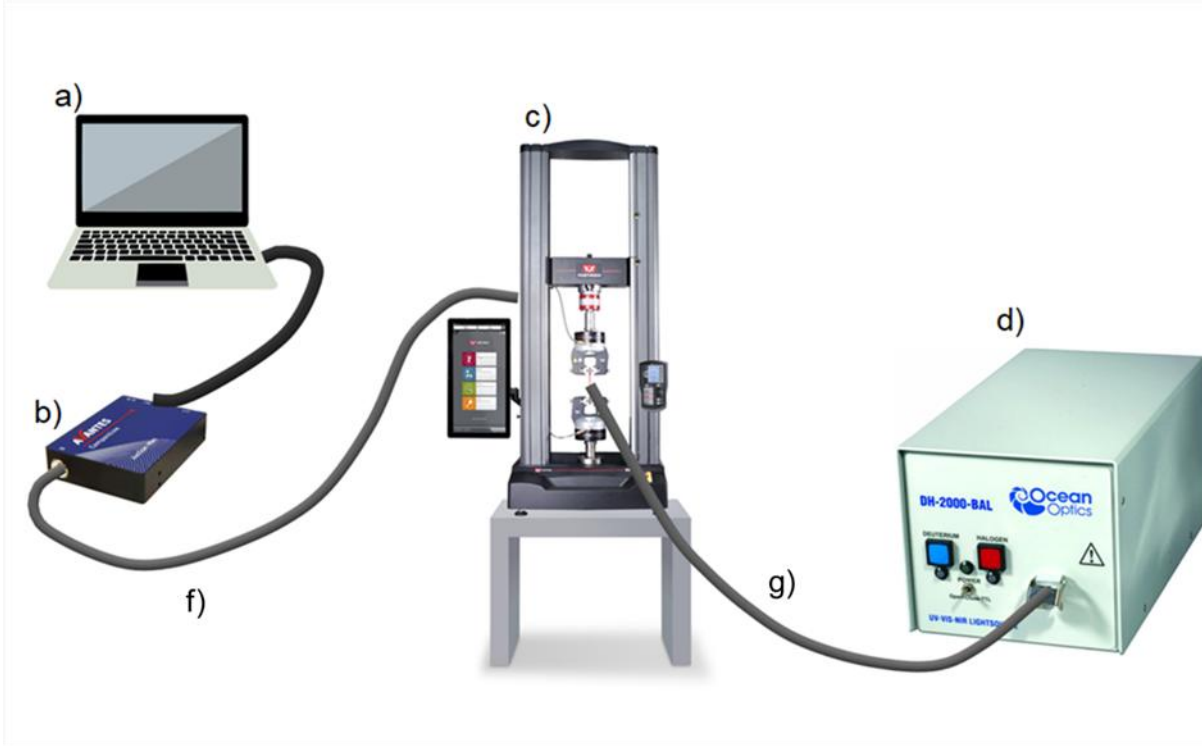


Figure A1.2: Custom-built optical fiber-based setup integrated with a tensile machine (Instron®5565) used for the optical-mechanical transmission measurements. The entire system consists of analysis software (a), a UV-VIS spectrometer (b), tensile machine (c), a deuterium-tungsten halogen light source (d), and a UV-vis-NIR optical fiber (f and g). The sample was docked to the Instron® original clamps.

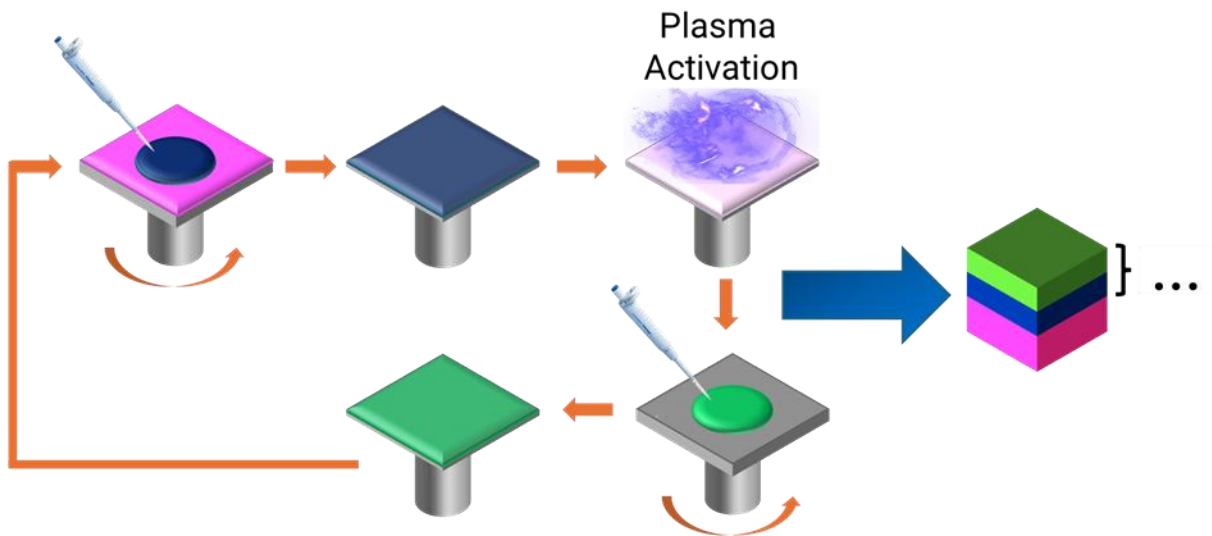


Figure A1.3: General Fabrication Method for Stretchable Photonic Structures via dynamic spin coating.

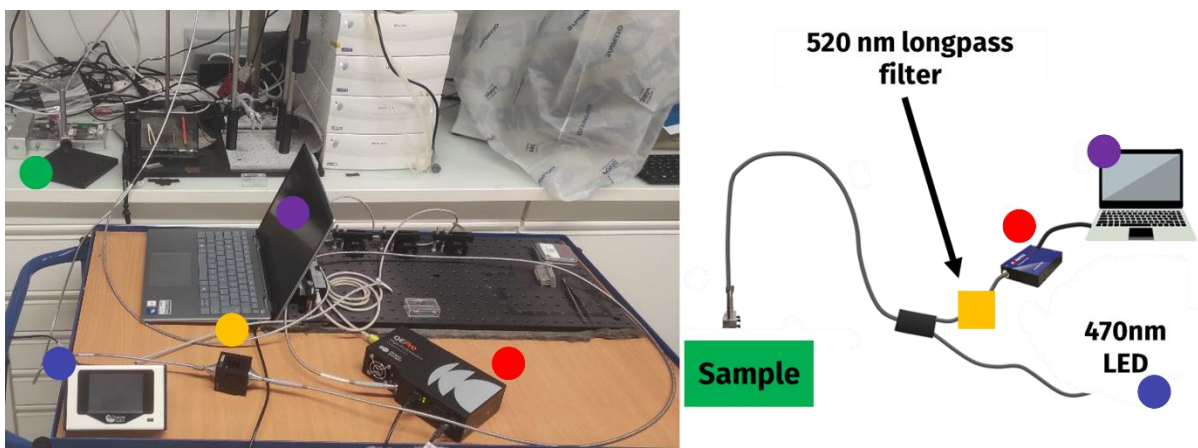


Figure A1.4: Schematic of the Strain-dependent Fluorescence Measurement set up including the 470 nm LED light source (blue circle), the sample in the microtensile stage (green rectangle), the 520 nm longpass filter (yellow square), the detector (red circle) and the laptop (violet circle).

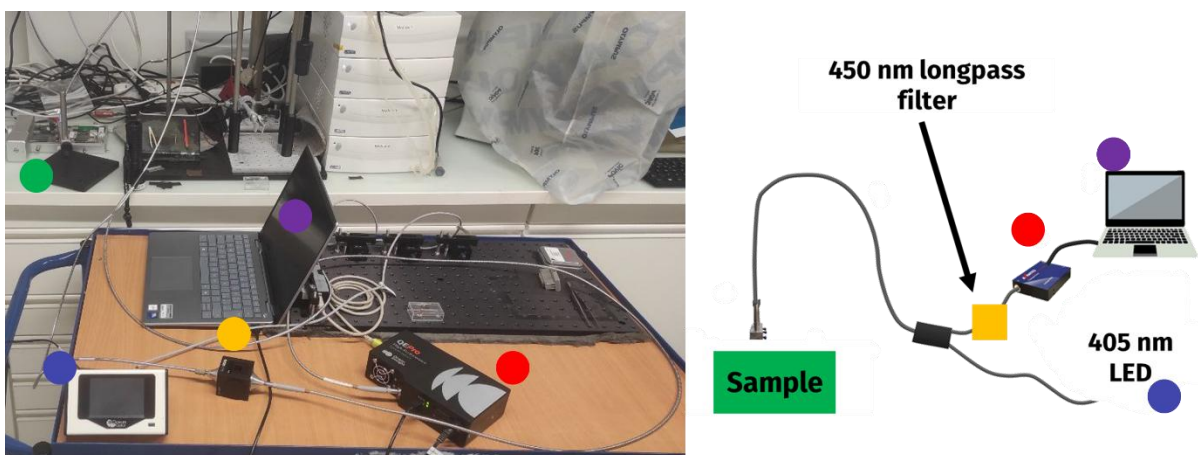


Figure A1.5: Schematic of the Strain-dependent Fluorescence Measurement set up including the 405 nm LED light source (blue circle), the sample in the microtensile stage (green rectangle), the 450 nm longpass filter (yellow square), the detector (red circle) and the laptop (violet circle).

Appendix 2: Photonic Chocolate

Since the fundamental concepts of photonics have already been discussed extensively in earlier chapters of this thesis, they will not be revisited in detail here. Instead, the following section focuses on how these principles were translated into an outreach activity developed during my PhD. Photonic materials have attracted wide interest due to the vivid structural colors observed in natural systems such as butterfly wings, peacock feathers, and beetle shells. These effects arise from nanostructures, ranging from diffraction gratings to hierarchical photonic architectures, that generate coloration through interference, diffraction, and reflection rather than pigments. Although these mechanisms are central to photonics education, the fabrication of ordered nanostructures is not typically accessible in introductory teaching environments, limiting the possibility of demonstrating these phenomena in a tangible way.

To address this limitation, during my PhD I developed an outreach activity based on an idea initially proposed by a former colleague (Dr. Heba Megahd), aimed at illustrating photonic principles through the use of “photonic chocolate.” Chocolate offers a suitable medium because its optical response can be modified by imprinting diffraction gratings onto properly tempered surfaces. This process requires the formation of a stable crystalline phase of cocoa butter, whose polymorphic behaviour determines the gloss and smoothness necessary for replicating micro- and nanoscale patterns. Beyond its optical relevance, the activity also provides a practical framework to introduce rheological aspects of chocolate, including its non-Newtonian shear-thinning properties and the influence of fat content, particle-size distribution, emulsifiers, and temperature on viscosity and mouthfeel. These characteristics make chocolate an unexpectedly rich material for demonstrating interdisciplinary concepts that lie at the intersection of optics, soft matter, and food science (Figure A2.1).

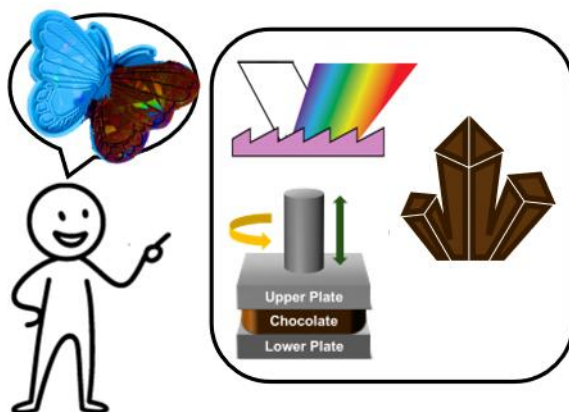


Figure A2.1: Schematic of the educational method “Photonic Chocolate”.

The seminars were structured to begin with a concise overview of key optical concepts, diffraction, interference, and structural coloration, illustrated through familiar natural and technological examples such as butterfly wings, holographic foils, and anti-counterfeiting features. This introductory section was followed by a discussion of chocolate tempering, emphasizing the polymorphism of cocoa butter and the necessity of forming a stable crystalline phase to obtain a smooth, reflective surface capable of accommodating a diffraction-grating pattern. The seminar then introduced the rheological behaviour of chocolate, highlighting its non-Newtonian, shear-thinning nature and explaining how factors such as fat content, particle-size distribution, emulsifier concentration, and temperature collectively influence viscosity and mouthfeel. The content and level of detail were adjusted according to the audience, allowing the activity to be effectively delivered to participants ranging from complete beginners to more advanced learners. This theoretical segment was followed by an explanation of chocolate tempering and the role of crystallization in achieving a surface suitable for grating replication. Participants then engaged in a hands-on session where they tempered chocolate and applied diffraction gratings, allowing a direct connection between the theory discussed and the resulting optical effects. Observing iridescence emerging on the chocolate surface helped participants immediately relate the practical outcome to the underlying photonic principles. One of these seminars was also presented as a science popularization event at the international EUPOC conference, providing an opportunity to share the activity with a broader scientific community. The overall initiative has been consolidated into a manuscript currently under review for publication in the ACS Journal of Chemical Education. Through the combination of materials science, optics, and food science, the photonic chocolate initiative provided an accessible platform for engaging audiences of different

backgrounds and ages, illustrating key principles of photonics through a familiar, tangible, and interactive medium.

Appendix 3: Communications

Publications:

- Martusciello M. et al., “Dip Coating Fabrication Of All-Polymer Multilayer Photonic Crystals Through 3D Printer Conversion” *ACS Appl. Polym. Mater.* 2025, 7, 4779–4786
- Martusciello M. et al., “Stretchable Distributed Bragg Reflectors as Strain-Responsive Mechanochromic Sensors” *ACS Appl. Mater. Interfaces.* 2024, 16, 51384-51396.
- L. Magnasco, M. Martusciello, A. Escher, G. Manfredi, P. Lova, D. Comoretto, A. Lanfranchi, “Polymer Planar Microcavities with CdSe-ZnS Core-Shell Quantum Dots for Label-Free Vapor Sensing” *Responsive Mater.* 2025, 3, e70017.
- Megahd, H., Carlotti, M., Martusciello, M., Magnasco, L., Pucci, A., Comoretto, D. and Lova, P., “Controlled Molecular Diffusion in Fluorescent Polymer Films for Label-Free Detection of Volatile Organic Compounds” *Adv. Sensor Res.* 2024, 3: 2300114.
- Magnasco, L.; Lanfranchi, A.; Martusciello, M.; Megahd, H.; Manfredi, G.; Lova, P.; Koszarna, B.; Gryko, D.; Comoretto, D.; "Fluorimetric Detection of Vapour Pollutants with Diketopyrrolopyrrole Polymer Microcavities" *ACS Omega* 2024, 9, 41, 42375–42385
- Martusciello M. et al., “Photonic Chocolate: A Sweet Holistic Playground to Explain Crystallization, Phase Transitions, Rheology, and Optics” (assigned to editor for *ACS Journal of Chemical Education*)
- Insogna R.; Martorelli F.; Di Fonzo D.; Martusciello M.; Utzeri R.; Angelini A.; Comoretto D.; Stagnaro P.; "Novel Sulfur-rich polymers from inverse vulcanization as functional building blocks for photonics" (Submitted to *Macromolecular Rapid Communications*)

Oral Communications:

- Martusciello, M.; Di Fonzo, D.; Lova, P.; Weder, C.; Comoretto, D.; Clough, J.; “Stimuli-Responsive Dyes In Stretchable Photonic Materials For Tunable Optical Functionality” *Macrogiovani* 2025, Pisa (PI), May 28th-30th, 2025
- Martusciello, M.; Lanfranchi, A.; Lova, P.; Comoretto, D.; “ Chameleon-Inspired 1D Photonic Crystals: Stretchable Photonic Sensors for Real-Time Strain Detection” *EUropean POlymer Conference “MacroLight” (EUPOC 2025)*, Bertinoro (Italy), May 11th-15th, 2025
- Martusciello, M.; Lanfranchi, A.; Castellano, M.; Lova, P.; Comoretto, D.; “Innovative Mechanochromic Photonic Crystals for Visual Strain Sensing” *XVIII Convegno Nazionale di Reologia*, Capri (NA), September 12th – 14th , 2024
- Martusciello, M.; Lanfranchi, A.; Castellano, M.; Lova, P.; Comoretto, D.; “Nature-inspired mechanochromic photonic crystals: advancements in distributed Bragg reflectors

for strain sensing” XXV Convegno Nazionale AIM, Napoli (NA), September 8th – 11th, 2024

- Martusciello, M.; Lanfranchi, A.; Lova, P.; Comoretto, D. “Refractive Resilience: Enhancing Mechanochromic DBRs Through a New Fabrication Approach” Macrogiovani 2024, Rimini (RN), June 12th-13th, 2024
- Martusciello, M.; Lanfranchi, A.; Castellano, M.; Lova, P.; Comoretto, D. “All-Polymer Based Mechanochromic Distributed Bragg Reflectors” Macrogiovani 2023, Catania (CT), June 21-23, 2023;
- Martusciello, M.; Lanfranchi, A.; Castellano, M.; Lova, P.; Comoretto, D. “Cristalli Fotonici Meccanocromici per la Sensoristica” Scuola di Chimica Industriale, Torino (TO), 28th May –1st June, 2023;
- Martusciello, M.; Lanfranchi, A.; Castellano, M.; Lova, P.; Comoretto, D. “Distributed Bragg Reflectors as Mechanochromic Sensors” “Polymer Metamaterials For Nanophotonics School - Mixing polymer chemistry, photonics and nanofabrication”,Claviere (IT), January 31st - February 2nd, 2023;
- Martusciello, M.; Lanfranchi, A.; Castellano, M.; Lova, P.; Comoretto, D. "Photonic Crystals Based On Block Copolymers As Mechanochromic Sensors For Structural Applications" EUropean POLYmer Conference (EUPOC) 2022 on “Block Copolymers: Building Blocks for Nanotechnology”, Bertinoro (IT), May 15th-19th 2022;
- Martusciello, M.; Lanfranchi, A.; Castellano, M.; Lova, P.; Comoretto, D. "Photonic Crystals Based On Elastomers As Mechanochromic Sensors For Structural Applications" Macrogiovani 2021, Genova (IT), July 21th-22th 2021

Poster Communications:

- Martusciello, M.; Di Fonzo, D.; Spinoso, V.; Martinez-Bueno, A.; D’Agostino, V.; Lanfranchi, A.; Lova, P. “Nanostructured Photocatalytic Films For Selective Pollutant Sorption And Light Harvesting Enhancement” Macrogiovani 2025, Pisa (PI), May 28th-30th, 2025
- Comoretto, D.; Martusciello, M.; Lova, P.; Weder C.; Clough J. “ Sculpting Light: Photochromic and Mechanochromic Dyes Embedded in Strain-Sensitive Polymer Nanostructures” EUropean POLYmer Conference “MacroLight” (EUPOC 2025), Bertinoro (Italy), May 11th-15th, 2025
- Martusciello, M.; Lanfranchi, A.; Castellano, M.; Lova, P.; Comoretto, D. “ Mechanochromic Photonic Crystals And Their Optomechanical Characterization”; PhD Day of Doctoral School in Sciences and Technologies of Chemistry and Materials, Genova (GE, Italy), February 15th – 16th 2024;
- Martusciello M., Lanfranchi A., Zago S., Magnasco L., Escher A., Bertucci S, Martorelli F., Megahd H., Comoretto D., Lova P. “Solution Processed Polymer and Hybrid Nanostructures for Sustainable Photonics”;14th International Conference on Optical Probes of Organic and Hybrid Semiconductors, Como (IT), September 10th-15th 2023;

- Martusciello, M.; Lanfranchi, A.; Castellano, M.; Lova, P.; Comoretto, D. “Optomechanical Characterization Of Mechanochromic Photonic Crystals”; 14th International Conference on Optical Probes of Organic and Hybrid Semiconductors, Como (IT), September 10th-15th 2023;
- Martusciello M., Lanfranchi A., Zago S., Magnasco L., Escher A., Bertucci S, Martorelli F., Megahd H., Comoretto D., Lova P. “Responsive Polymer and Solution Processed Nanophotonics” Macrogiovani 2023, Catania (CT), June 21-23, 2023;

Awards:

- Best presentation award during Macrogiovani 2025, Pisa (PI), May 28th-30th, 2025
- Best poster award during PhD Day of Doctoral School in Sciences and Technologies of Chemistry and Materials, Genova (GE, Italy), February 15th – 16th 2024;
- Third best oral presentation at “Scuola di Chimica Industriale”, Torino (TO), May 28th – June 1st, 2023;
- Best poster award sponsored by Royal Society of Chemistry at the 14th International Conference on Optical Probes of Organic and Hybrid Semiconductors, Como (CO), September 10-15th, 2023

