

Lamellar structure formed from block copolymer for structural color

Yiquan Wang *

Shanghai Foreign Language School Affiliated to SISU, Shanghai, China

* Corresponding Author Email: wyqoscar2163.com

Abstract. Certain brilliant colors in living species, such as, in plants, animals, insects, fungi, seaweed, and so on, known as structural colors, have attracted tremendous attention from researchers worldwide. Block copolymers are an interesting class of material that has been proven effective in fabricating structural colors due to their capability to self-assemble into structures on the scale of the wavelength of visible light. Lamellar structure is one of these structures. The demand on the high-quality structural colors in large scale application requires the easy modification of commercial block copolymers to obtain structural colors. In this project, a method to easily prepare structural colors is presented. First, an already commercialized block polymer was purchased. Then, the block copolymer is mixed with the small molecule guest to prepare a supramolecular complex solution. By slowly evaporating the solution, these supramolecular complexes can be assembled into a lamellar structure that displays structural color. By changing the ratio of polymer to small molecular guest and using different small molecular guests, polymer films of different colors can be obtained and tuned.

Keywords: block copolymer; lamellar structure; structural color; supramolecular interaction.

1. Introduction

Color is prevalent in nature, attracting many scientists to investigate it and the artificial materials that demonstrate it. In nature, many species have incredibly brilliant colors, such as plants, animals, insects, fungus, seaweeds, etc.[1-3]. These colors are produced not by small-molecule dyes, but by the interaction of their surface structure with sunlight. Such colors are known as structural colors, and their discovery has aroused the interest of researchers all around the world. Through systematic studies, researchers have discovered that the optical processes of interference, diffraction or scattering of light caused by the neatly arranged micron or nanostructures on the surfaces of these species are the source of the colors [4-6]. Unlike pigments and dyes, such structured colors are not affected by photobleaching or photoquenching effects and can therefore be used for long periods of time. In addition, their non-toxic nature makes them suitable for biological and medicinal applications. Therefore, there has long been a great interest in artificial photonic materials with structural colors.

Among the many photonic materials with different structures, Among the numerous photonic materials with various topologies, lamellar structures have received a lot of interest due to their simple structure and bright and vivid colors. Block copolymers, which can self-assemble structures with scales in the visible wavelength range, have shown to be an efficient and practical way for producing structural colors. Such structures are known as one-dimensional photonic crystals. Not all block copolymers are appropriate for the building of one-dimensional photonic crystals. Several of them have been demonstrated to have no photonic characteristics. To determine the parameters required for structural color, the mechanism of color generation in one-dimensional photonic crystals should be elucidated first. It is commonly assumed that the colors shown by one-dimensional photonic crystals are formed by multilayer interference of reflected light at each contact between the layered structures. A typical one-dimensional photonic crystal is made up of two periodically alternating materials with different refractive indices, as shown in Figure 1.

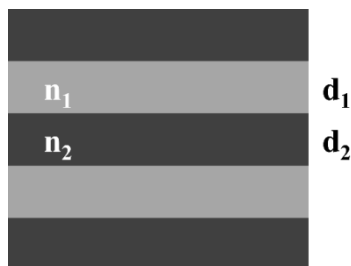


Figure 1. Typical one-dimensional photonic crystal.

At the boundary of each layer, the incident light can be reflected or transmitted. When the thickness of the layer is comparable to the wavelength of the incident light, the light reflected from different surfaces interferes with each other in length or extinction, thus enhancing or reducing the reflected light at that wavelength. When the reflected wavelength is in the visible light range, it can be observed as a structural color. More specifically, according to Bragg-Snell law, the wavelength of the reflected light (λ) can be described as a function of the layer thickness (d), the refractive index (n_{eff}) and the angle of incidence (θ) as shown in Equation 1 [7-11] .

$$m\lambda = 2d\sqrt{n_{eff}^2 - \sin^2 \theta} \quad (1)$$

In Equation 1, m is the order of diffraction. It is worth noting that n_{eff} is the effective refractive index in a one-dimensional photonic crystal as

$$n_{eff} = \frac{(n_1 d_1 + n_2 d_2)}{(d_1 + d_2)} \quad (2)$$

In Equation 2, d_1 and d_2 are the thicknesses of the layers in a bilayer, and n_1 and n_2 are their respective refractive indices. In a one-dimensional photonic crystal, the periodic domain is defined as the interplanar spacing D , which is the sum of the thicknesses of the two layers ($D = d_1 + d_2$).

For a non-absorbing material with normal incidence ($\theta = 0$), Equation 1 can be simplified as

$$m\lambda = 2(n_1 d_1 + n_2 d_2) \quad (3)$$

As shown in Equation 3, for a given combination of materials, the color displayed by the film is determined by the thickness of the two layers. Thus, by adjusting the refractive index and layer thickness, the wavelength of light reflection can be adjusted to the visible window.

In the case of block copolymer-based photonics, the layer thickness depends primarily on the length scale of each block within the block copolymer. If the polymer chains of these blocks are short or not fully stretched, the domain spacing of their assembled structures will not be sufficient to interact with visible light. This is the main factor why some block copolymers with well-defined laminar structures do not show any color. In order for these structures to show color, parameters in terms of refractive index or layer thickness can be optimized. During the last two decades, numerous researchers have developed many strategies to achieve this goal. In general, the composition and structure of the block copolymers can be adjusted by chemical synthesis, which can change the size of the assembled layer structures, which in turn can modulate the preparation to obtain different colors. However, this method requires complex synthesis and repetitive experimental operations, which greatly hinders the development of photonic materials based on block copolymer layered structures. In recent years, researchers have discovered that by doping and stimulating block copolymers and their constituent structures, they can easily modulate the colors. These findings show great advantages in the preparation and adjustment of structural colors. For example, materials with high refractive index are added into certain layers to improve their optical properties, while homopolymers or solvents are used to extend the domain spacing of these layers. [12-17] However, the need for high-quality structural colors for use in broader scenarios still requires more exploration and discovery of modulations and their corresponding polymeric materials.

In this research, a conventional, readily available, commercial block polymer was used. The supramolecular composite solution can be prepared by simply adding small molecule guests. After

evaporation of the solvent, the solution can form a lamellar structure with structural color. By simply adjusting the ratio of polymer to small molecule guests, the prepared structural color can be obtained in different colors. In addition, different guest molecules have been used to investigate the effectiveness of different molecules to form supramolecular complexes and structural colors.

2. Experimental part

2.1. Materials

Polystyrene-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP) was purchased from Polymer Source. 4-Dodecylbenzenesulfonic acid (DBSA, $\geq 95\%$), 3-*n*-pentadecylphenol (PDP, $\geq 97.0\%$ (GC)), and chloroform were purchased from Sigma-Aldrich. All materials were used directly without further purification.

2.2. Preparation method

PS-*b*-P2VP and DBSA were dissolved separately in chloroform, placed in small containers, and left for one day before usage. The two solutions were mixed in a certain ratio to form a series of supramolecular complexes, stirred overnight, and set aside. The solutions were formed into thin films in the containers using the dip coating technique. The films were left at room temperature so that the solution could evaporate slowly.

The mole ratios were DBSA:2VP = 0.5, 1.0, 2.0, 5.0.

PS-*b*-P2VP and PDP were dissolved separately in chloroform, placed in small containers, and left for one day before usage. The two solutions were mixed in a certain ratio to form a series of supramolecular complexes, stirred overnight, and set aside. The solutions were formed into thin films in the containers using the dip coating technique. The films were left at room temperature so that the solution could evaporate slowly.

The mole ratio is PDP:2VP = 0.2, 0.4, 0.8

2.3. Characterization methods

2.3.1 Molecular characterization of polymers

^1H NMR Spectroscopy characterization: PS-*b*-P2VP polymer was dissolved in CDCl_3 . The hydrogen spectra signals were recorded using a ^1H NMR spectrometer (Bruker AVANCE NEO 400 MHz).

Gel Permeation Chromatographic characterization: The samples were dissolved in THF at a concentration of 1 mg/mL. The sample efflux time and signal intensity were recorded using a gel permeation chromatography (Waters 1515, column system: PLMIXED 7.5x50 mm guard column and two PLMIXED-C 7.5X300 chromatographic columns). The molecular weight and polydispersity were obtained with reference to polystyrene standard samples.

2.3.2 Characterization of PS-*b*-P2VP and DBSA, PDP interactions

^1H NMR spectroscopy characterization: PS-*b*-P2VP and PDP, DBSA were dissolved in CDCl_3 , and the samples were mixed according to the proportions in Experiments 2.2.1 and 2.2.2 above, left overnight, and the hydrogen spectral signals of the samples were recorded using a ^1H NMR spectrometer.

Infrared (IR) spectroscopic characterization: The interaction of PS-*b*-P2VP with DBSA was studied using an infrared spectrometer (Thermo Nicolet 6700) at room temperature. The corresponding supramolecular solutions described above were added dropwise to potassium bromide crystals. The films were placed in an oven and dried under vacuum overnight, and the samples were then analyzed using an infrared spectrometer. The wave number range was from 800 to 4000 cm^{-1} , the accuracy of the tested wave number was from 4 to 8 cm^{-1} , and the number of scans was 32.

2.3.3 Structural color characterization of polymeric films

Camera recording of film color: use the camera to record sample color in bright locations.

UV-Vis-NIR spectroscopic characterization: The prepared films were placed in the UV-Vis-NIR spectrometer (Lamda 950) and the reflection spectra of each sample were tested. The wavelengths tested ranged from 400 nm to 800 nm.

Atomic force microscopy (AFM) characterization: The film surface was characterized using an atomic force microscope (Bruker DIMENSION ICON) in TAPPING test mode to observe the lamellar structure and record pictures of the sample morphology.

3. Experimental results and discussion

3.1. Characterization of the polymers used

First, we characterized the information of the polymer. The ^1H NMR spectra of the polymers are shown in Figure 2. The proton signal at the o position of P2VP is located near 8.2 ppm, and the signals of P2VP at the m, n, and l positions and PS at the i, j, and k positions overlap together and appear near 7.0 ppm. The integral ratio of the proton signal at 8.2 ppm to the proton signal at 7 ppm is 3.69/45.97 (Figure 2). This ratio of signals represents the ratio of the number of hydrogen atoms at the two positions. From the molecular formula, the ratio of the number of hydrogen atoms at these two locations is $y/(5x+3y)$. Therefore, it can be derived that $y/(5x+3y) = 3.69/45.97$. In addition, the molecular weight of the polymer can be obtained by gel permeation chromatography characterization. As shown in Figure 3, the molecular weight of the block polymer is 512476 g/mol, then $512479 = 104.15x + 105.14y$. Combining the result from ^1H NMR hydrogen spectra and the gel permeation chromatography, we can infer that the degree of polymerization of PS is 3208 and that of P2VP is 1696, so the polymer can be expressed as $\text{PS}_{3208}\text{-b-P2VP}_{1696}$.

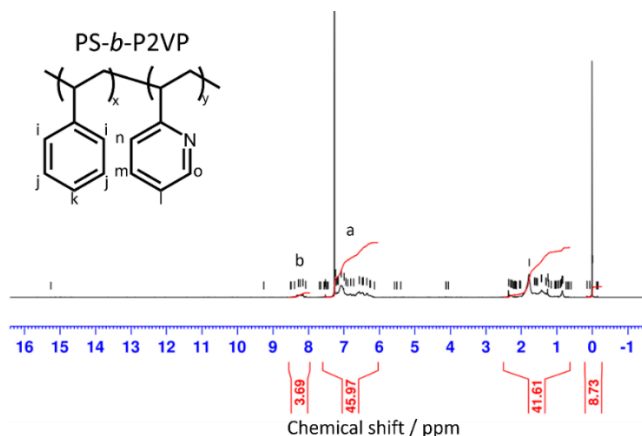


Figure 2. ^1H NMR spectra of the polymers.

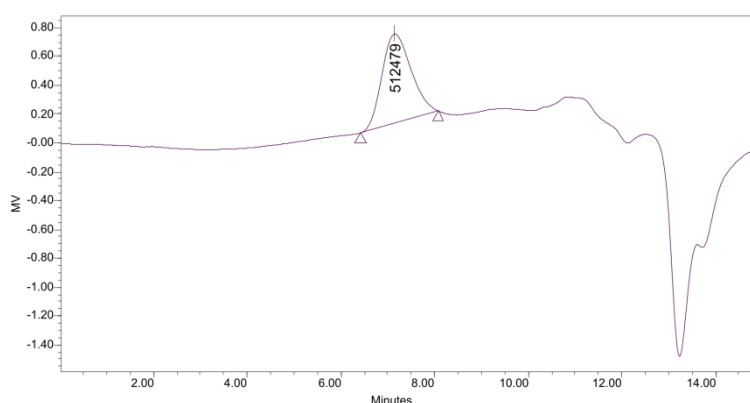


Figure 3. Gel permeation chromatography signal profiles of the polymers.

3.2. Characterization of supramolecular complex interactions

From 3.1, the polymer can be represented as PS₃₂₀₈-*b*-P2VP₁₆₉₆, so the corresponding chain segments of PS and P2VP are not of the same length, and it is difficult to obtain a one-dimensional lamellar structure if the polymer molecule is used directly for the assembly of the membrane material. Therefore, as designed, we use small molecules to modify the P2VP portion of the shorter chain segment of the polymer, and the N atoms on the P2VP can form supramolecular complexes with other small molecules to increase the size of this chain segment. Here we have chosen dodecylbenzenesulfonic acid (DBSA) as the ligand molecule, which can form supramolecular complexes with the polymer through hydrogen bonding and ionic interactions. The occurrence of these interactions can be determined by characterization through ¹H NMR spectroscopy and IR spectroscopy. As shown in Figure 4, the proton signal located near 8.0 ppm is attributed to the signal of the hydrogen atom adjacent to the nitrogen atom in P2VP. With the addition of DBSA, a splitting of the signal here can be observed. The degree of cleavage gradually increases with increasing the amount of DBSA. In addition, the proton signal of DBSA located near 11.0 ppm disappears when DBSA is added to PS-*b*-P2VP. The proton signal in P2VP located near 6.5 ppm gradually decreased with the increase of the amount of DBSA. In addition, once DBSA was added to PS-*b*-P2VP, a new proton signal attributed to NH was generated near 3.5 ppm. With the addition of more amounts of DBSA, this signal was gradually displaced from 3.5 ppm to 4.5 ppm to 5.5 ppm. All data above demonstrate the combination of DBSA and P2VP.

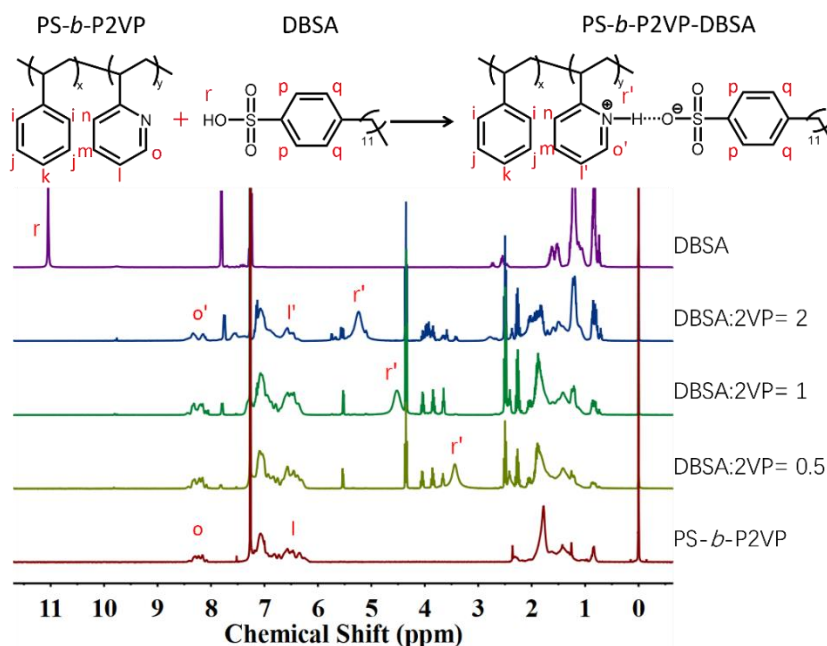


Figure 4. Characterization of the nuclear magnetic resonance hydrogen spectrum of PS-*b*-P2VP interacting with DBSA supramolecules.

In addition, IR spectra was used to demonstrate the occurrence of the interaction. As shown in Figure 5, the characteristic signals of PS-*b*-P2VP appear at 1589, 1566, 1475, 1435, 750, 695, and 543 cm⁻¹. The signals of DBSA appear at 1170, 1129, 1007, 829, and 581 cm⁻¹. After the addition of DBSA to PS-*b*-P2VP, its signals at 1589 and 1566 cm⁻¹ disappeared and a new signal appeared at 1737 cm⁻¹, which was attributed to the protonated P2VP. In addition, we also observed the disappearance of the signals at 750, 695, and 543 cm⁻¹, the weakening of the signals at 1475 and 1435 cm⁻¹, the corresponding new signal at 606 cm⁻¹, and the strengthening of the signal at 1373 cm⁻¹. All these changes in the IR spectra indicate the interaction of PS-*b*-P2VP with DBSA. In addition, for DBSA, its signal disappears at positions 1170, 1129, 1007, and 581 cm⁻¹, indicating a change in the proton on DBSA after binding to PS-*b*-P2VP.

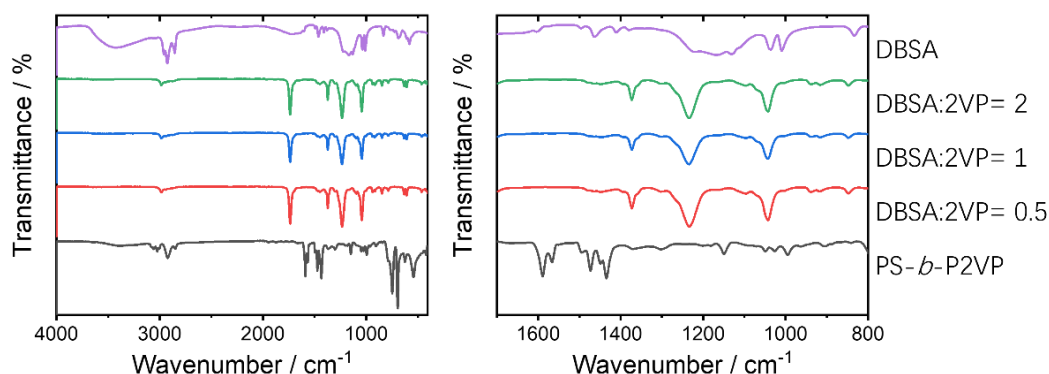


Figure 5. Infrared spectral characterization of the interaction of PS-*b*-P2VP with DBSA supramolecules.

3.3. Preparation of sample films with structural color

It is clear from the above that PS-*b*-P2VP can indeed supramolecularly interact with DBSA. The preparation of structurally colored sample films using this supramolecular complex became our next goal. Following the method reported in the literature [18], the polymer solution slowly formed a film after one week at a low temperature of 4 °C. Considering its long experimental time and the huge energy consumption involved, we tried to improve the sample preparation method and develop an effective method for the preparation of structurally colored films suitable for our system.

First, we used a glass sheet with a white coating on the back, as in Figure 6a to increase the color contrast and to ensure that color formation could be detected and monitored in a timely manner. The solvent evaporated rapidly (~10 s) into a film using a dropper to add a mixture of solutions on its surface, however, no color was observed. After analyzing the reasons, we concluded that the film formation time was too short and the block polymer chain segments did not have enough time to self-assemble into a lamellar film, allowing no color to be observed. Then, we refer to the experimental operation of thin-layer chromatography by placing the glass sheet in a container and filling it with solvent vapor in advance, as in Figure 6b. We hope that this method will slow down the evaporation of the solvent and allow time for the polymer segments to move and assemble. The film formation time was about 5 minutes, which greatly reduced the solvent evaporation rate and extended the polymer movement and assembly time, however, we still did not observe color production.

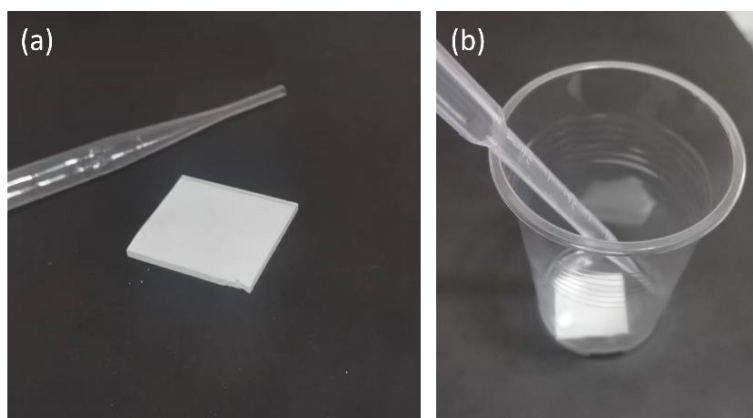


Figure 6. Diagram of the apparatus for the investigation of the sample film preparation method.

To further attenuate the rate of solvent evaporation, we used a 10 mL sample bottle with a small hole left in the cap as in Figure 7, put the mixed solution into the bottom and left it for 12 h. After 12 h, all solvent evaporation was completed and the polymer formed a thin film. The films showed color, which proved that prolonging the solvent evaporation time could promote the assembly of the polymer and obtain the structural color. However, another problem was noted: the color was not uniform and the film could not be removed from the bottom of the bottle even after the sample bottle

was cut horizontally using a glass cutter because the thickness was too thin. Finally, we used a 2 mL sample bottle, reduced the volume of the container, still drilled a small hole in the cap, put the mixed solution into it, and let it stand for 24 hours before the solution evaporated into a film. The films appeared more uniform in color and we will use this method to prepare polymer films and characterize polymer film color in subsequent investigations.

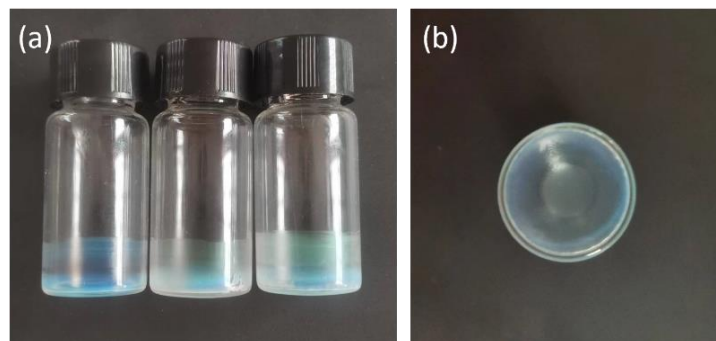


Figure 7. Preparation of structural color films using sample vials.

3.4. Structural color of supramolecular complexes

Based on the optimization of the film preparation method above, we finally successfully prepared the sample films with good morphology, as shown in Figure 8. By changing the ratio of the molar mass of DBSA to 2VP repeating units in PS-*b*-P2VP (from DBSA:2VP = 0.5 to DBSA:2VP = 2), we could obtain supramolecular composite films with different colors and observed a color change from blue to indigo to green. We then characterized the UV-Vis-NIR spectra of these polymer films to probe and determine the reflection spectra of these films. It is known from the spectra that with the addition of more DBSA, the reflection peaks of the polymer films were red-shifted from 430 nm (DBSA:2VP = 0.5) to 460 nm (DBSA:2VP = 1) to 525 nm (DBSA:2VP = 2). We also performed AFM characterization of these polymer films as shown in Figure 9. From Figure 9, we can clearly see the formation of the lamellar structure. This proves that the addition of the DBSA small molecule effectively increases the size of the P2VP chain segment, making the PS chain segment comparable in size to the P2VP chain segment, which in turn induces them to form lamellar structures. These findings can be further confirmed by the characterization of Scanning Electron Microscopy. As shown in Figure 10, for the supramolecular complexes with DBSA:2VP = 0.5 and 1, we clearly observe that the domain spacing of their lamellar structures is 147 and 156 nm, respectively, and the increase of the domain spacing explains the red shift of the reflection peaks of the reflectance spectra, and these values are in good agreement with the theoretical estimates obtained from Equation 3. All these results justify the rationality and validity of our use of supramolecular complexes for the preparation of lamellar structures and the color of the structures.

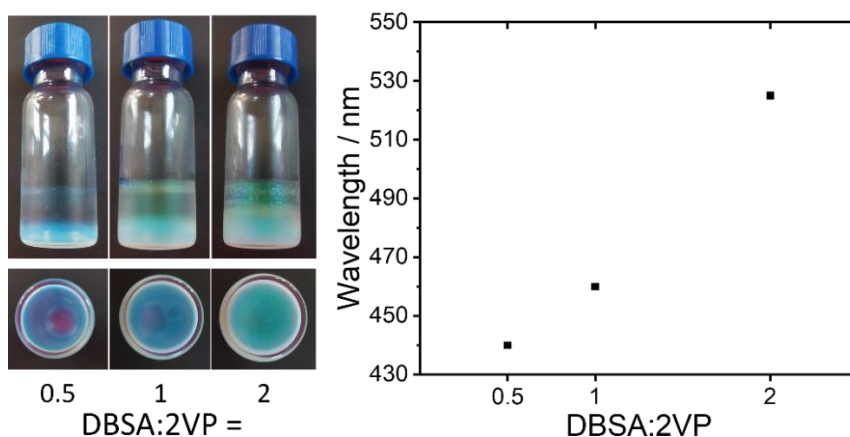


Figure 8. Structural color and wavelength vs. ratio relationship of PS-*b*-P2VP and DBSA supramolecular complexes.

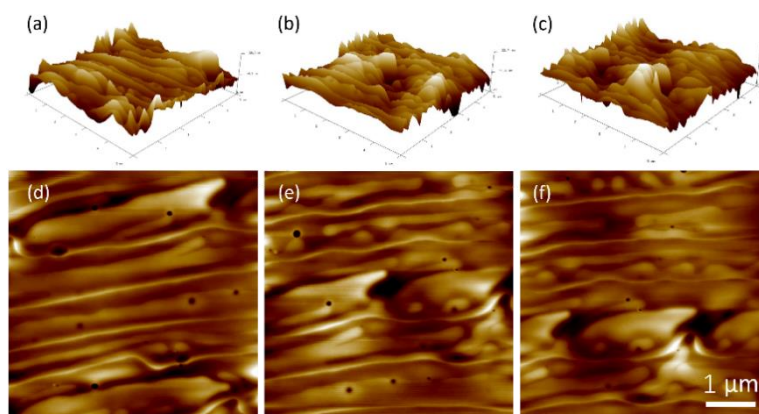


Figure 9. AFM mapping of PS-*b*-P2VP in supramolecular complex with DBSA.

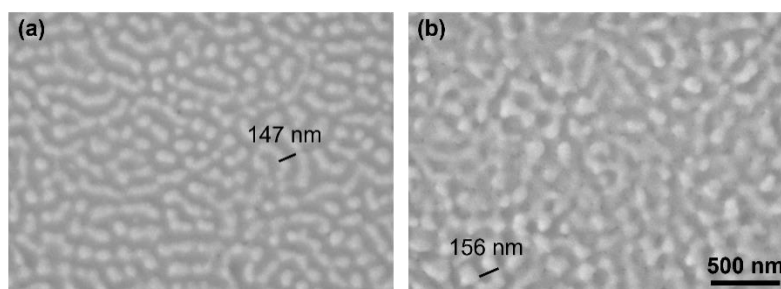


Figure 10. Scanning electron microscopy mapping of PS-*b*-P2VP in supramolecular complex with DBSA.

The change in the peak of the reflected spectrum is due to the fact that when more DBSA is added to the PS-*b*-P2VP solution, the size of the P2VP chain segment portion increases due to the formation of more supramolecular interactions. The larger P2VP domain spacing causes an increase in the overall domain spacing of the lamellar structures formed by PS-*b*-P2VP, and according to Equations 1 and 3, they reflect a corresponding red-shift in spectral color. All these structures demonstrate that supramolecular interactions can effectively increase the polymer chain segment size. It also supports our design and expectation of this experiment to change the domain spacing of the lamellar structure by varying the amount of the incorporated molecule guests, which in turn results in a change in the color of the structure of this polymer film from no apparent color to blue to green.

To further our understanding and application of this system, another small molecule guest, 3-*n*-pentadecylphenol (PDP, Figure 11a), was also used to increase its size by combining with the P2VP portion of PS-*b*-P2VP. Based on the ^1H NMR hydrogen spectra (Figure 11c), it is known that PDP can successfully form supramolecular interactions with PS-*b*-P2VP. Such supramolecular interactions assisted in the generation of structural colors, which were successfully prepared as shown in Figure 11b. From PDP:2VP = 0.2 to PDP:2VP = 0.8, the polymer films exhibit the same blue to green transition as that achieved using DBSA. It is noteworthy, however, that while the same color change is observed, the molar mass required when PDP is used is significantly less than that used with DBSA. This means that PDP can more efficiently achieve an increase in the lamellar structure of the polymer film formed by PS-*b*-P2VP. This is closely related to its molecular structure. As shown in Figure 11a, PDP has a longer alkyl terminus compared to DBSA. This means that when used in combination with P2VP, its longer alkyl side chains can expand the size of P2VP to a greater extent. The use of fewer molar mass of small molecule guests produces a change in the larger domain spacing that matches our observation that the same reflected wavelength structural color can be achieved using fewer molar mass of small molecules.

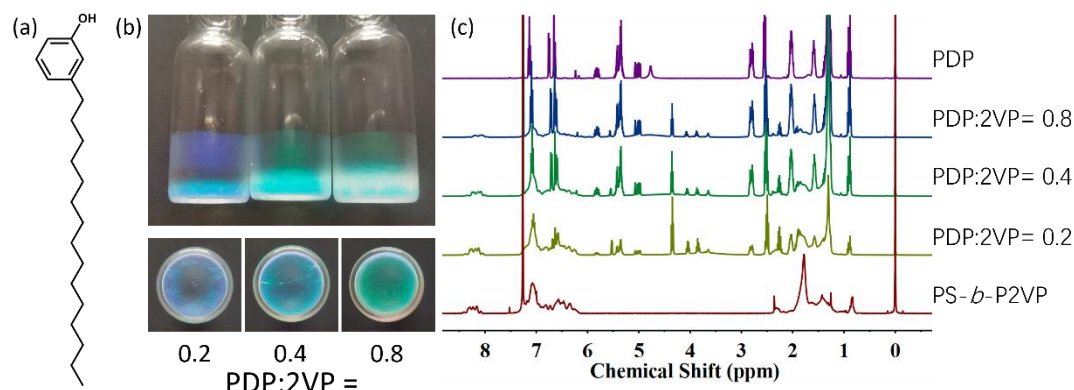


Figure 11. Characterization of ^1H NMR spectra of PS-*b*-P2VP supramolecular complexes with PDP and their colors.

4. Conclusion

In this project, we have successfully prepared a variety of structural colors including blue, indigo and green based on supramolecular interactions of polymers with small molecules. The polymers used can be easily prepared and are now available commercially, solving the problem of the source of raw materials for the preparation of structural colors using polymers. In addition, we were able to produce multiple colors using only one polymer, which demonstrates the feasibility, simplicity, and practicality of the supramolecular approach proposed in this project. These structural colors are produced due to the formation of lamellar structures, and when different amounts of small molecules are used, structures with different domain spacing can be produced. In addition, both DBSA and PDP have been used as small molecules to increase the domain spacing of the lamellar structures. PDP shows greater effectiveness in increasing the domain spacing due to the presence of longer alkyl structures.

Acknowledgements

I am very grateful to my supervisor for giving me the opportunity to complete this project and giving me careful guidance. I am grateful to my supervisor for allowing me to complete this assignment and for his thoughtful supervision. I am also thankful to my lab mates for their advice and assistance during the experimental phase, which provided me with a clear understanding of scientific research and helped me to decide the path I am interested in.

References

- [1] A. G. Dumanli and T. Savin, *Chem. Soc. Rev.* 2016, **45**, 6698-6724.
- [2] H. Fudouzi, *Sci. Technol. Adv. Mater.*, 2011, **12**, 064704
- [3] M. X. Kuang, J. X. Wang and L. Jiang, *Chem. Soc. Rev.* 2016, **45**, 6833-6854.
- [4] S. Kinoshita, S. Yoshioka and J. Miyazaki, *Rep. Prog. Phys.*, 2008, **71**, 076401.
- [5] Y. Fu, C. A. Tippets, E. U. Donev and R. Lopez, *W. I. Res. Nanomed. Nanobi.* 2016, **8**, 758-775.
- [6] S. Kinoshita and S. Yoshioka, *Chemphyschem*, 2005, **6**, 1442-1459.
- [7] S. Kinoshita and S. Yoshioka, *Chemphyschem*, 2005, **6**, 1442-1459.
- [8] J. Ge and Y. Yin, *Angew. Chem. Int. Ed.* 2011, **50**, 1492-1522.
- [9] A. L. Liberman-Martin, C. K. Chu and R. H. Grubbs, *Macromol. Rapid. Comm.* 2017, **38**, 1700058.
- [10] M. E. Calvo, S. Colodrero, N. Hidalgo, G. Lozano, C. Lopez-Lopez, O. Sanchez-Sobrado and H. Miguez, *Energy Environ. Sci.* 2011, **4**, 4800-4812.
- [11] H. Z. Shen, Z. H. Wang, Y. X. Wu and B. Yang, *RSC Adv.* 2016, **6**, 4505-4520.

- [12] Y. Kang, J. J. Walish, T. Gorishnyy and E. L. Thomas, *Nat. Mater.* 2007, **6**, 957-960.
- [13] Y. Kang, *B. Kor. Chem. Soc.*, 2008, **29**, 2329-2330.
- [14] S. E. Shin, S. Y. Kim and D. M. Shin, *J. Nanosci. Nanotechnol.* 2011, **11**, 4275-4278.
- [15] Y. Ahn, E. Kim, J. Hyon, C. Kang and Y. Kang, *Adv. Mater.* 2012, **24**, OP127-OP130.
- [16] H. S. Lim, J.-H. Lee, J. J. Walish and E. L. Thomas, *ACS Nano*, 2012, **6**, 8933-8939.
- [17] o. B. Ayyub, M. B. Ibrahim and P. Kofinas, *Polymer*, 2014, **55**, 6227-6231.
- [18] S. Valkama, H. Kosonen, J. Ruokolainen, T. Haatainen, M. Torkkeli, R. Serimaa, G. t. Brinke, O. Ikkala. *Nature Mater.* 2004, **3**, 872-876.