

Synthesis of Norbornene-Based Block Copolymers by Sequential Ring-Opening Metathesis Polymerization and Their Unique Optical Properties

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Norbornene-based block copolymers with macromolecular side chains such as polycaprolactone and polylactide were successfully synthesized via ring-opening metathesis polymerization using the third-generation Grubbs' initiator.

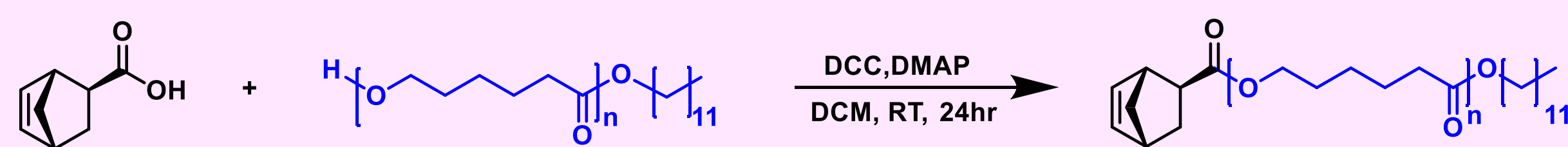
Introduction

Block copolymers have attracted much attention in recent years due to their unique self-assembly behavior that can be useful for the design and preparation of a diverse library of nanostructured materials [1]. Recent studies have demonstrated that the self-assembly process of the block copolymers can be controlled which can lead to novel optical properties [2]. In this study, norbornene-based homopolymers and block copolymers containing macromolecular side chains such as polycaprolactone and polylactide were successfully synthesized by ring-opening metathesis polymerization of their corresponding macromolecular monomers using the third generation Grubbs' initiator. Macromolecular monomers, such as norbornene-polycaprolactone and norbornene-polylactide, were prepared via Steglich esterification reaction catalyzed by dicyclohexylcarbodiimide and 4-dimethylaminopyridine. The optical properties and morphologies of the polymer thin films have been investigated.

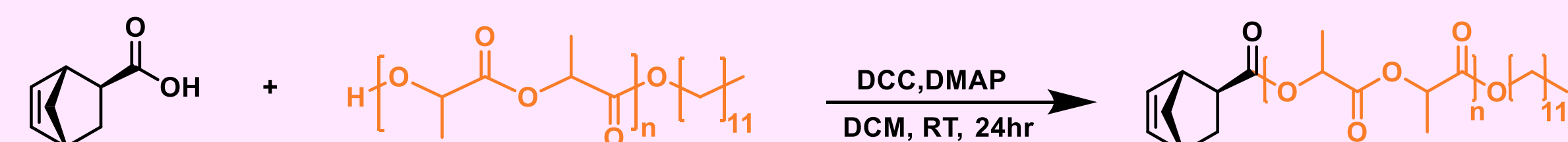
Synthesis

The synthetic routes to macromonomers **M1** and **M2** are shown below. The compounds were synthesized via Steglich esterification using **dicyclohexylcarbodiimide (DCC)** as the coupling agent and **4-dimethylaminopyridine (DMAP)** as the catalyst to promote ester bond formation between carboxylic acid and hydroxyl groups.

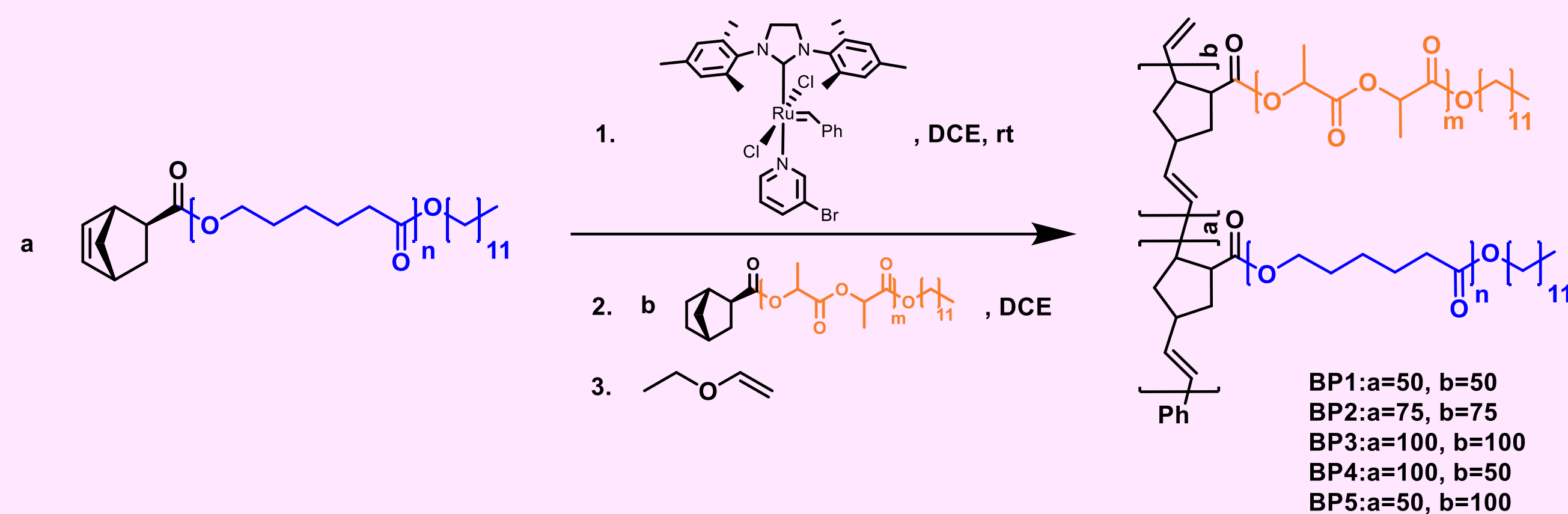
(a) NB-PCL (**M1**)



(b) NB-PLA (**M2**)



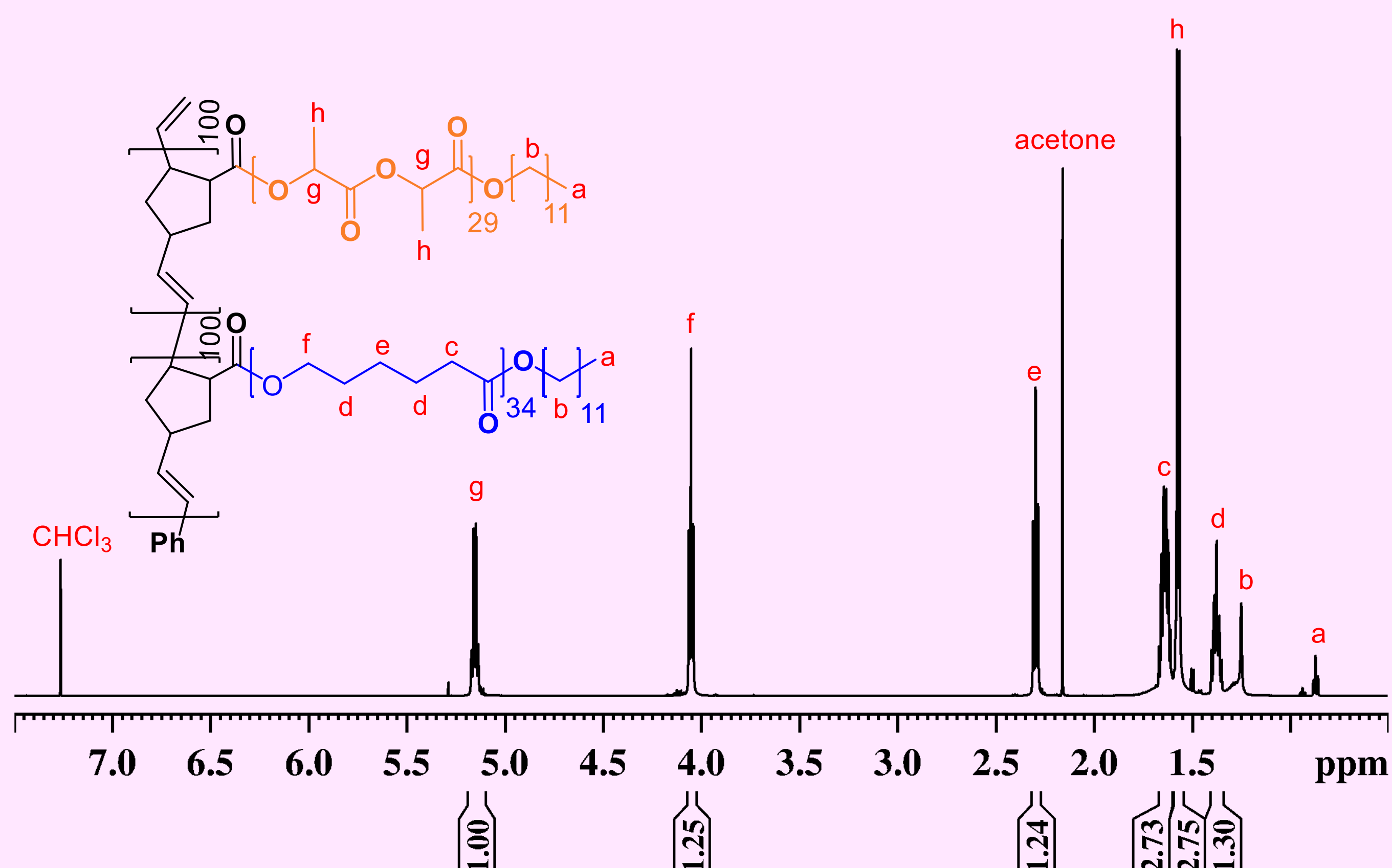
The macromonomer **M1** was dissolved in anhydrous DCE at a concentration of **0.05 M**. Subsequently, the G3 was added to initiate polymerization and the reaction mixture was stirred under an argon atmosphere at **room temperature** for **5 mins**. Following complete consumption of **M1**, the second macromonomer **M2** was added to the reaction at a concentration of **0.025 M** and the mixture was stirred for an additional **90 mins** at **50°C**.



¹H NMR Spectrum

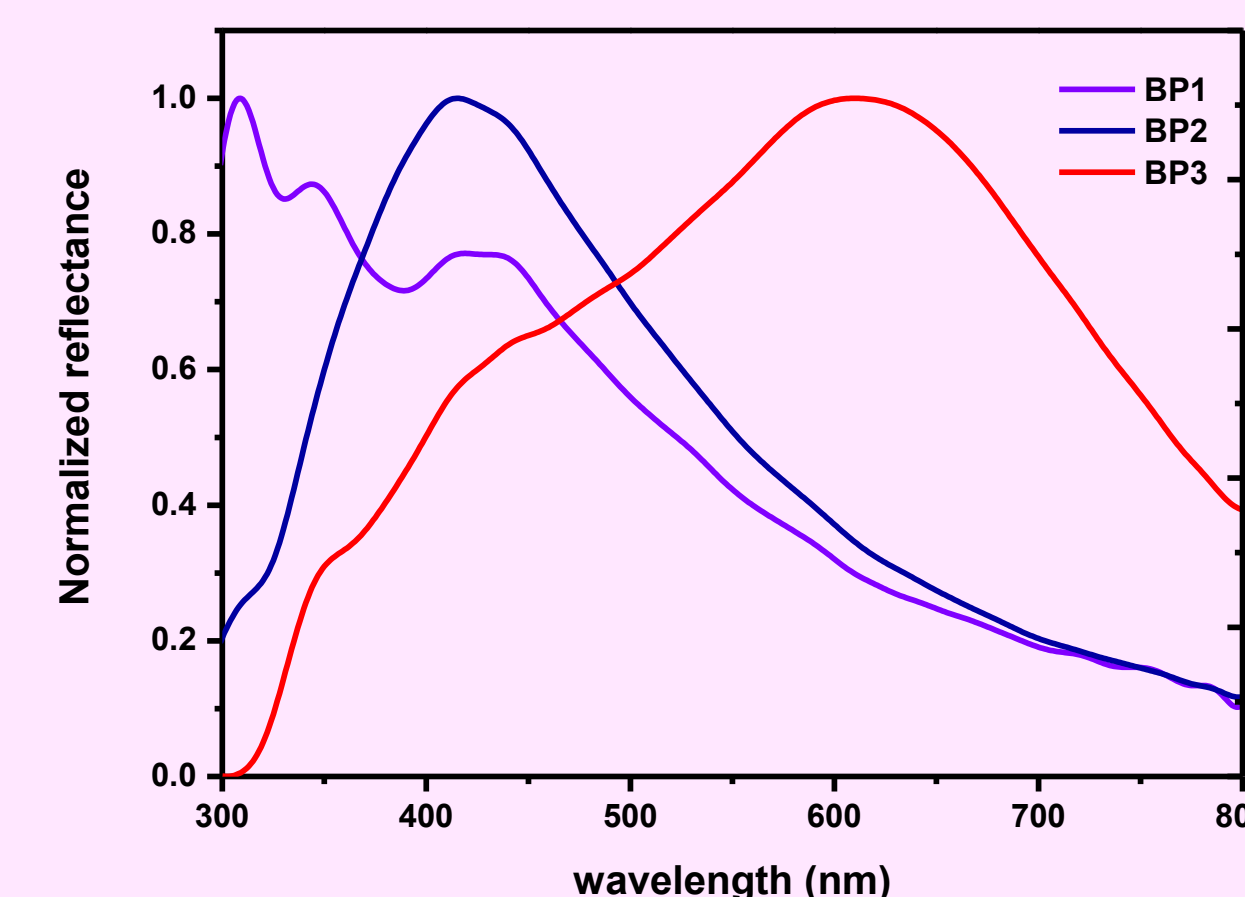
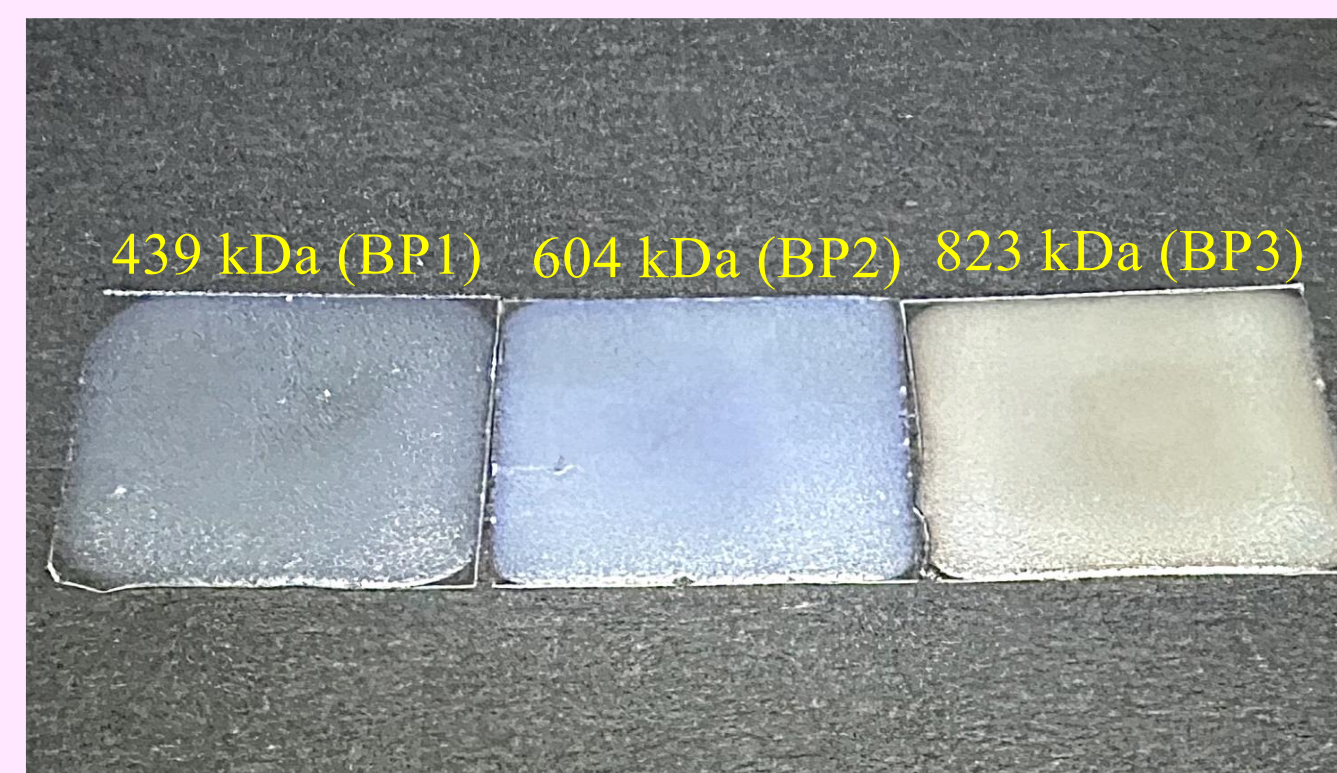
The ¹H NMR spectrum of block copolymer (**BP3**) was shown below. Signals are attributed to the hydrogens from the side chain of PLA and PCL. Chemical shifts of the hydrogens **H_c**, **H_d**, **H_e** and **H_f** in the **PCL** side chains appear as a triplet at 2.29 ppm, multiplets at 1.68–1.59 ppm as well as 1.41–1.33 ppm and a triplet at 4.05 ppm, respectively. While the quartet at 5.18–5.13 and doublet at 1.57 ppm are associated with hydrogens **H_g** and **H_h** from **PLA**. Furthermore, the integration values of **H_f** and **H_g** which correspond to the methylene hydrogens in PCL in PLA, respectively were further used to calculate the block ratio.

The molecular weights and polydispersity indices (PDI) of **BP1** to **BP5** were determined by gel permeation chromatography (GPC) at 45°C. The PDI of all polymers is close to 1.1, indicating a narrow molecular weight distribution and uniform polymer chain lengths.

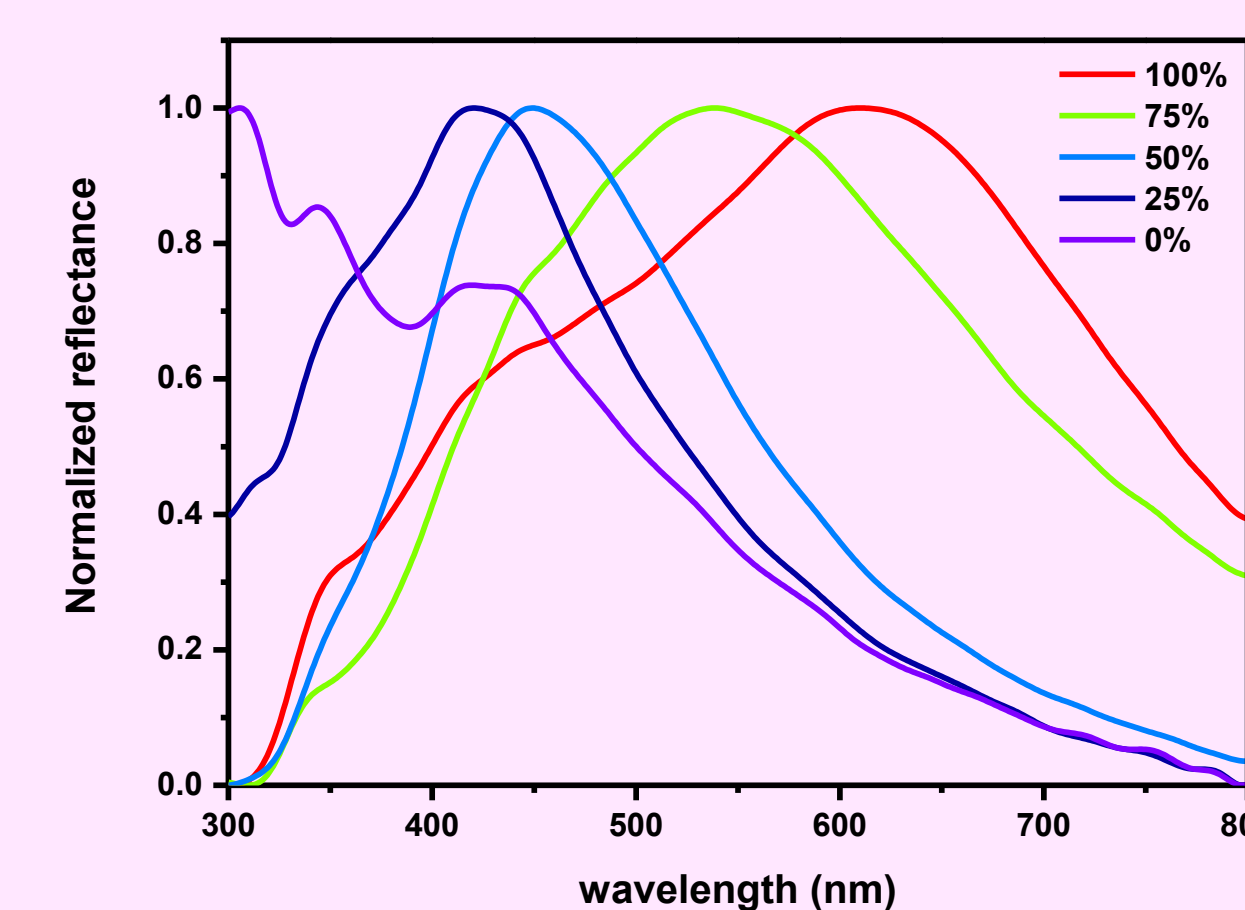
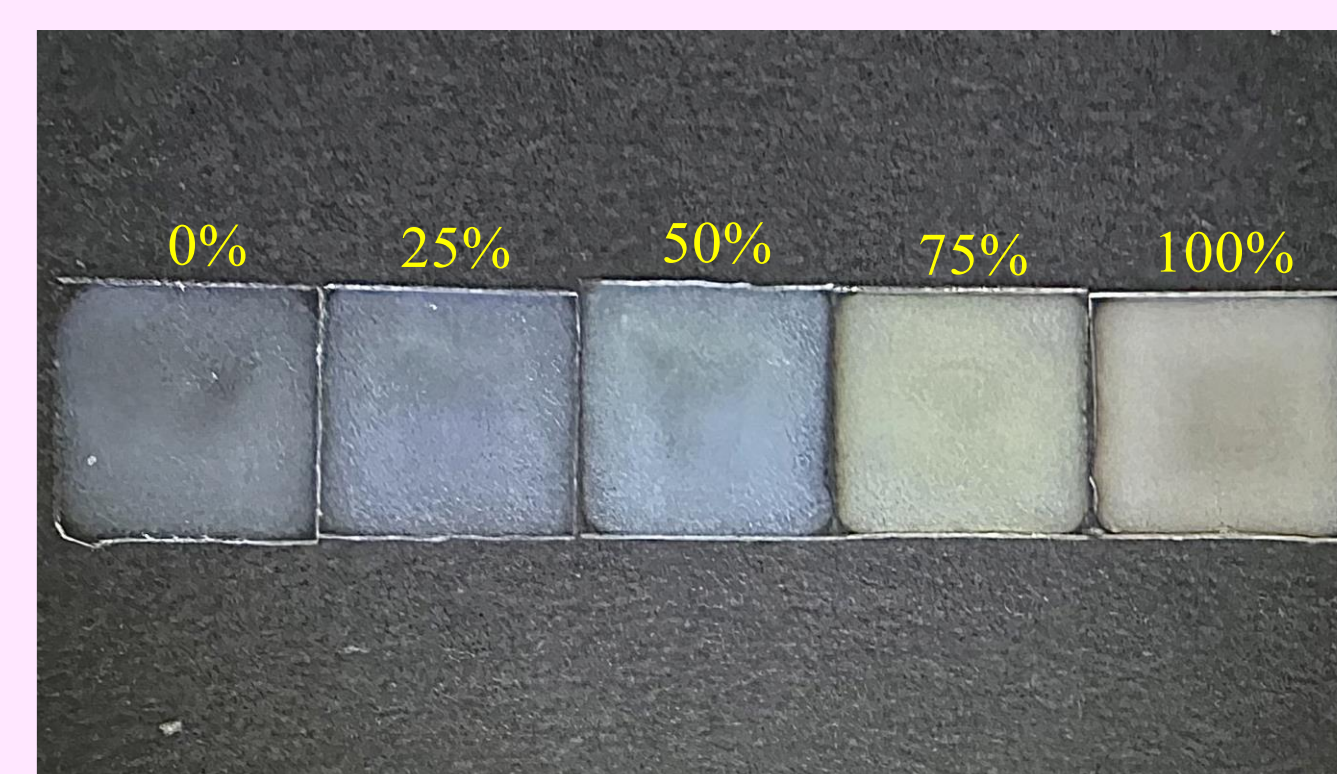


Optical Properties of Photonic Crystals

The reflectance spectra and corresponding film photograph are shown below. A clear red-shift in the reflection wavelength can be observed with increasing molecular weights of the polymers. **BP1** (lowest molecular weight) exhibited maximum reflection wavelength (λ_{max}) at **305 nm**, with relatively low reflectivity. While λ_{max} of **BP2** and **BP3** is at 415 nm and 610 nm, respectively. These results suggest that polymers with higher molecular weights promotes greater bottlebrush chain extension, thereby facilitating long-range structural ordering and the formation of periodic nanostructures.

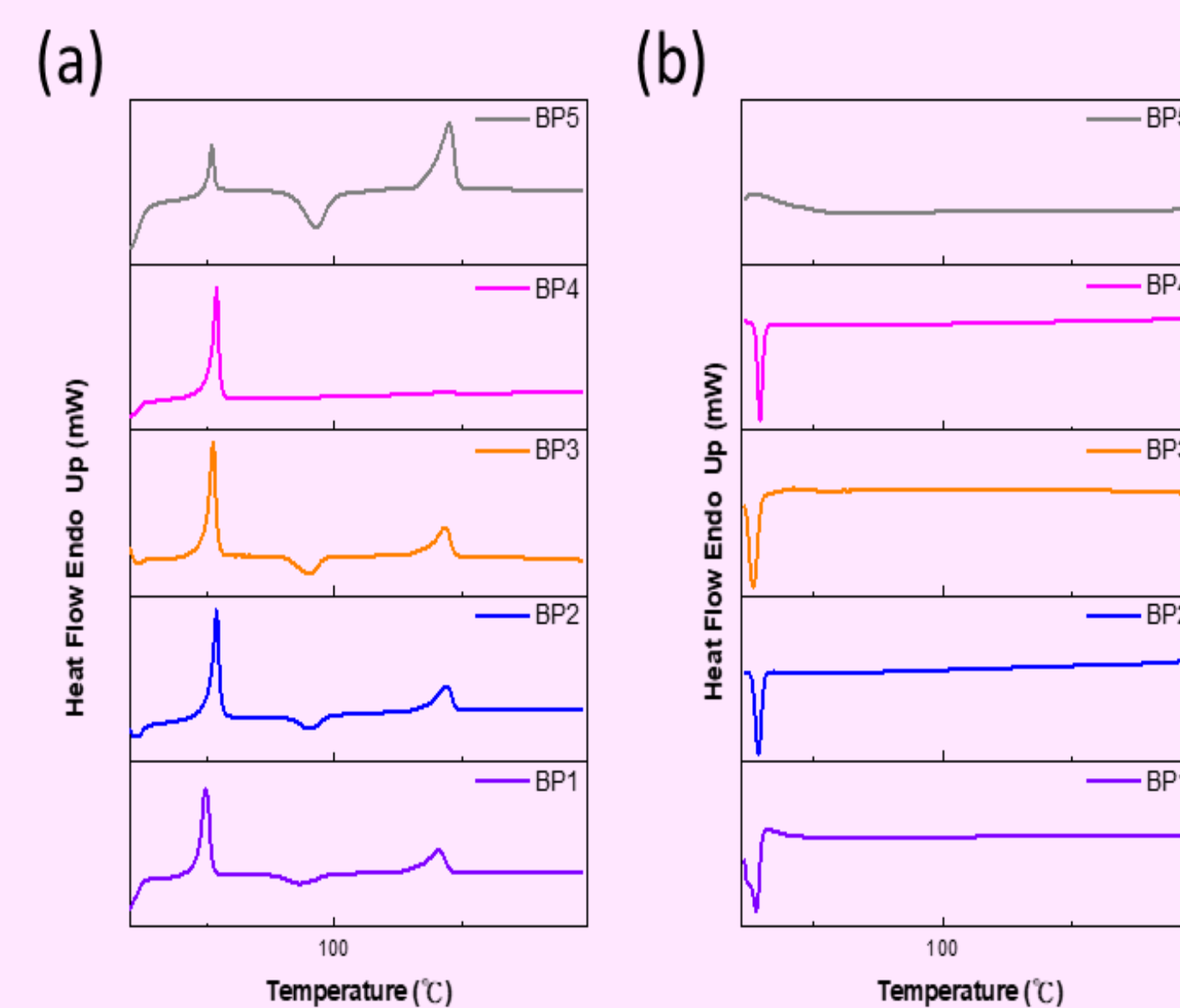
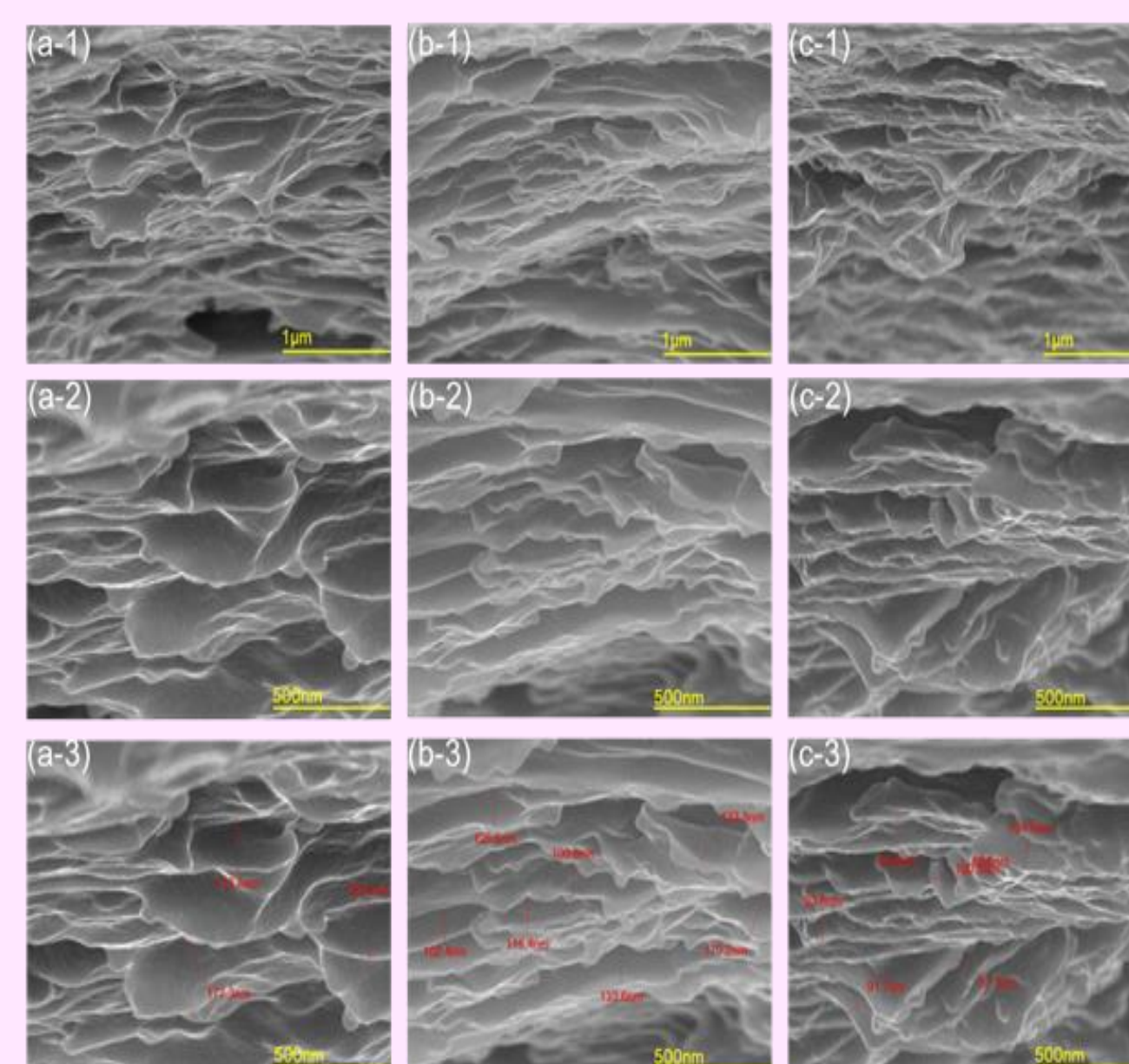


For binary blend system, as the **BP3** content increases, the reflection wavelength gradually red-shifts from **305 nm** (pure **BP1**) to **610 nm** (pure **BP3**) with a corresponding visible color from blue to red. This systematic shift is attributed to changes in the periodic spacing of the self-assembled nanostructures. **BP3** with a higher molecular weight contributes to thicker lamellar domains and longer periodicity, resulting in longer reflection wavelength. These results demonstrate that the photonic band gap can be effectively tuned by the blend ratio of two polymers.



SEM Images and DSC Traces

SEM images of **BP1**, **BP2** and **BP3** clearly demonstrate lamellar architectures with progressively increasing D-spacing. The measured D-spacing expands from approximately **85–105 nm** in **BP1**, to **100–130 nm** in **BP2**, and further to **173–192 nm** in **BP3**, suggesting the effect of different molecular weights of the polymers. This trend is strongly associated with the reflectance, which transitions from 305 nm in BP1 to 415 nm in BP2 and 610 nm in BP3. The result demonstrates that longer D-spacing leads to longer reflection wavelength.



Conclusions

In this study, bottlebrush block copolymers containing polycaprolactone and polylactide side chains were successfully synthesized and fully characterized. Binary blend of two block copolymers at varying weight percentages exhibit the maximum reflectance wavelength ranging from 305 nm to 610 nm.

References

- [1] Mai, Y.; Eisenberg, A.; Self-assembly of block copolymers. Chem. Soc. Rev. 2012, 41, 5969-5985. DOI: 10.1039/c2cs35115c.
- [2] He, Q.; Ku, K. H.; Vijayamohanan, H.; Kim, B. J.; Swager, T. M.; Switchable Full-Color Reflective Photonic Ellipsoidal Particles. J. Am. Chem. Soc. 2020, 142, 10424-10430. https://doi.org/10.1021/jacs.0c02398.