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## Polymeric One-Dimensional Reflectors Based on Self-Organization of Comb-Shaped Supramolecules

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### ABSTRACT

Polystyrene-*block*-poly(4-vinylpyridine) (PS-*block*-P4VP) diblock copolymer was complexed with dodecylbenzenesulfonic acid (DBSA), leading to comb-coil polymeric supramolecules PS-*block*-P4VP(DBSA)<sub>y</sub> ( $y = 1.0, 1.5, \text{ and } 2.0$ ). Complexes formed hierarchical lamellar structure with long period of ca. 1400 Å. Due to periodicity and refractive index contrast between the layers, transmission and reflectance measurements showed a relatively narrow incomplete bandgap at ca. 460 nm. The angular dependence of the bandgap was also studied using different angles ( $\theta$ ) relative to the surface normal. The mid-gap was blue-shifted when the incident angle was increased indicating that the lamellar structure was partly oriented by the surfaces of quartz glasses.

### INTRODUCTION

The manipulation the flow of light using periodic dielectric structures has received much attention over the recent years [1-2]. Photonic crystals are long-range ordered structures whose dielectric constant varies periodically. Under certain conditions (with a suitable structure and a sufficient dielectric contrast), photonic crystals may exhibit a forbidden bandgap within which no photons will be allowed to propagate [1]. In combination with controlled defect structures, a wealth of applications in photonics is expected: e.g. capability to confine, guide and control light.

Such photonic crystals are not straightforward to construct. Detailed structures and defects, in principle, are possible to construct with sufficient dielectric contrast using lithographic and etching techniques but achievement of small structures down to the optical length scale is challenging. Spontaneous assemblies of colloids [3], synthetic opals [4-7], inverted opals [4,8-10], and block copolymers [11-14], on the other hand, allow the preparation of small enough structures. Although self-assembly leads to a well-defined local order and offers a low-cost method for the production of photonic crystals, it is nontrivial to achieve perfectly ordered structure with carefully engineered defects over the macroscopic length scale [15].

Block copolymers can self-organize into a wide variety of periodic structures (e.g. lamellar (1D), cylindrical (2D), spherical, and gyroid (3D)) typically at a length scale of 100 – 1000 Å, i.e. smaller than the optical length scale [15]. Increase in the long period up to 1000 – 2000 Å range, corresponding to  $\lambda/2n$  for optical wavelengths could, in principle, be achieved just by using block copolymers of higher molecular weight. This, however, would lead to excessively

slow structure formation and poor structures are expected. Narrow molecular weight homopolymers or oligomeric plasticizers [12-13] can be added in order to swell the block copolymer domains. In this way, incomplete photonic bandgaps have been constructed where increased dielectric contrast has been achieved in some cases by incorporating suitable high refractive index inorganic additives within the domains [11].

Comb-shaped polymeric supramolecules [16] consisting of hydrogen bonded “combs” (alkyl phenols) within one block of a polystyrene-*block*-poly(4-vinylpyridine) diblock copolymer has been shown to lead structure-*within*-structure self-organization with particularly long period due to stretching of the chains [17]. Importantly, the structure formation is particularly facile as the hydrogen bonded phenolic side chains, in addition of being constituents of the supramolecules, simultaneously act as plasticizers. This may offer significant benefits, since block copolymers usually demand specific procedures to obtain well-developed local structures.

Here we selected polystyrene-*block*-poly(4-vinylpyridine) with dodecylbenzenesulfonic acid (DBSA) “combs” leading to comb-coil supramolecules PS-*block*-P4VP(DBSA)<sub>y</sub>. In the stoichiometric composition PS-*block*-P4VP(DBSA)<sub>1.0</sub>, DBSA-molecules are expected to be bonded to the pyridines by protonation and further DBSA can be hydrogen bonded to the sulphonates of the inner P4VP(DBSA)<sub>1.0</sub> layer.

## EXPERIMENTAL DETAILS

PS-*block*-P4VP diblock copolymer was supplied by Polymer Source Inc. ( $M_{n,PS} = 238,100$  g/mol,  $M_{n,P4VP} = 49,500$  g/mol,  $M_w/M_n = 1.23$ ) and dodecylbenzenesulfonic acid (DBSA) was purchased from Tokyo Kasei (90 %). Materials were used without further purification. Both PS-*block*-P4VP and DBSA were dissolved in chloroform (Riedel-de Hæn, 99 %) separately and the homogenous solutions were combined leading to complexes PS-*block*-P4VP(DBSA)<sub>y</sub>. Here  $y$  denotes the number of DBSA groups vs. 4-vinylpyridine repeat unit ( $y = 0, 1.0, 1.5, \text{ and } 2.0$ ). Solutions were stirred 24 hours and solvent was slowly evaporated at 4 °C. Thereafter the samples were vacuum dried at 60 °C for 48 hours. For measurements as a function of an incident angle samples were prepared between two quartz glasses in order to decrease the surface roughness. Thickness of samples was of the order of 100 μm (estimation is based on the sample weights and the substrate area).

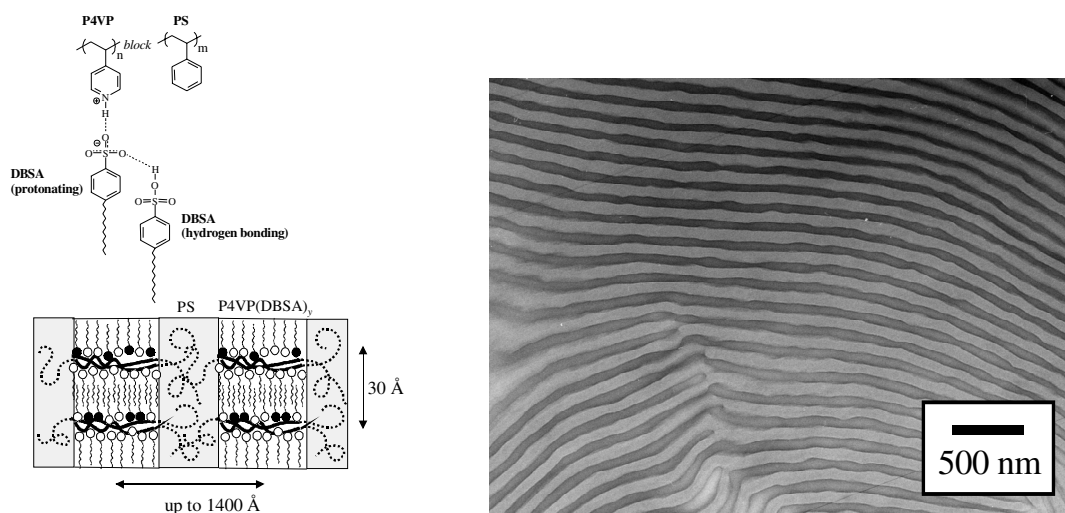
For transmission electron microscopy (TEM) characterization ultra thin sections (approximately 70 nm) were cryomicrotomed at – 160 °C using a Leica Ultracut UCT-ultramicrotome and a Diatome-diamond knife. Dry sections were stained for 5-7 hours in vapors of I<sub>2</sub> crystals. Bright-field TEM was performed on JEOL-2000FX transmission electron microscope operating at an accelerating voltage of 200 kV.

The angular dependence of the bandgap was measured by Hitachi U-2000 double beam spectrophotometer in the wavelength range 200 – 1000 nm. Spectral diffuse reflectance and transmission were measured in the wavelength range 300 – 950 nm. The angle of incidence was 8 degrees and light was collected with an integrating sphere detection system over the entire hemisphere [14].

## DISCUSSION

Pyridine and DBSA are a strong base and acid, respectively, and when they are mixed in solution, charge transfers from the acid to the lone electron pair of pyridine is expected to take

place. FTIR measurements showed that due to the protonation the carbon-nitrogen stretching band of P4VP at ca.  $1597\text{ cm}^{-1}$  is shifted to  $1639\text{ cm}^{-1}$ , which corresponds to protonated P4VP [14,18]. The interaction between P4VP and DBSA makes possible the formation of well-defined comb-coil supramolecular structures due to repulsion between the charged backbone and the nonpolar alkyl tails. Combining supramolecular entities to the self-organization of block copolymers leads to hierarchical structures (the lamellae-*within*-lamellae structure is schematically represented in Figure 1). The lamellar structure of PS-*block*-P4VP(DBSA)<sub>2,0</sub> with a long period of ca.  $1400\text{ \AA}$  is represented in Figure 1. Smaller internal structure in P4VP(DBSA)<sub>2,0</sub> was not resolved in TEM. Due to the I<sub>2</sub> staining, the P4VP(DBSA)<sub>2,0</sub> layer appear dark in the image.



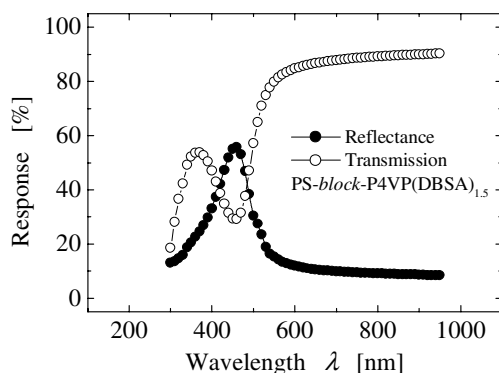
**Figure 1.** Schematics of interactions between PS-*block*-P4VP and DBSA and hierarchical lamellae-*within*-lamellae structure. Note that part of the DBSA molecules can be hydrogen bonded instead of protonated. TEM micrograph of complex PS-*block*-P4VP(DBSA)<sub>2,0</sub> illustrating the lamellar structure with a long period ca.  $1400\text{ \AA}$ . The P4VP(DBSA)<sub>2,0</sub> layer shows dark in the image due to I<sub>2</sub> staining.

The structures and their periodicities were also characterized with X-ray scattering in  $q$ -range of  $0.004 - 2.0\text{ \AA}^{-1}$  for  $\lambda = 1.54\text{ \AA}$  (data is not shown here). The pure PS-*block*-P4VP has a shoulder at ca.  $0.009\text{ \AA}^{-1}$  corresponding to structure with long period of ca.  $700\text{ \AA}$ , but a precise determination of the morphology is impossible due to the absence of higher order peaks. The complex with  $y = 1.5$  has the first intensity maximum at  $q^* = 0.0050\text{ \AA}^{-1}$  with resolvable third, fifth and seventh order peaks. This indicates a relatively well-developed lamellar structure with a long period of  $1300\text{ \AA}$ . Lamellar structure is also expected because the weight fraction of PS in the complex is  $w = 0.46$ .

Pure DBSA is an isotropic fluid and it has only a broad correlation hole maximum centered at  $q^* = 0.31\text{ \AA}^{-1}$  corresponding to the long period of ca.  $20\text{ \AA}$ . Complexes, on the other hand, have more organized structures within the P4VP(DBSA)<sub>y</sub>-domains resulting from the repulsion between the charged P4VP-backbone and the nonpolar dodecyl side chain (see Figure 1). A narrow first order intensity maximum is observed at  $0.21\text{ \AA}^{-1}$  ( $L_p = 30\text{ \AA}$ ). However, the morphology of these structures could not be determined due to the lack of higher order peaks.

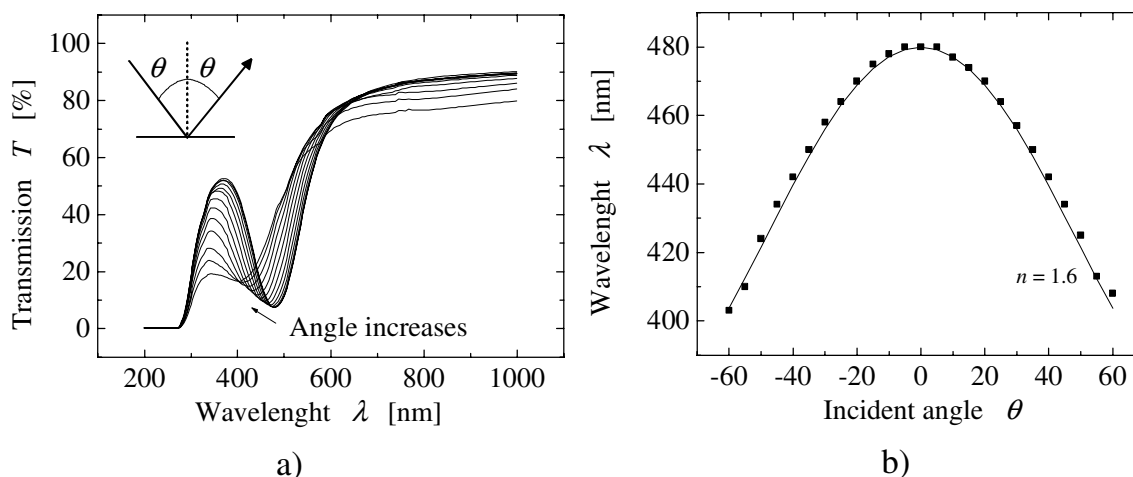
The simplest example of photonic crystals is a multi-layer stack. However, they will not lead to a complete photonic bandgap due to their 1D structure. Incident light is reflected from each interface between the layers and the position of the mid-gap is determined by the optical thickness of structure. The amount of the reflected light, in turn, depends on the number of layers as well as on the refractive index contrast between them. In our case, the long periods of the multi-layer stack, consisting of alternating PS- and P4VP(DBSA)<sub>y</sub>-layers, are comparable to  $\lambda/2n$  of light. Refractive index contrast between polymer layers is usually small and also due to the lack of macroscopic orientation and the variation in long periods, a complete bandgap is difficult to fulfil using polymers.

Figure 2 shows the diffusive transmission and reflectance curves in the wavelength range 300 – 950 nm for complex PS-*block*-P4VP(DBSA)<sub>1.5</sub> (Note, that pure DBSA and the uncomplexed PS-*block*-P4VP block copolymers are strongly absorbing below ca. 280 nm but they have high transmission above it [17]). PS-*block*-P4VP(DBSA)<sub>1.5</sub>, in turn, has an incomplete and fairly narrow bandgap at ca. 460 nm (the relative width of the reflectivity peak,  $\Delta\lambda/\lambda$ , is ca. 0.20). The position of the mid-gap qualitatively agrees with the long period of sample ( $\lambda/2n$  condition) based on TEM and X-ray scattering studies. Typically the refractive index  $n$  of these kinds of polymers is of the order 1.5 – 1.6, which explains the narrowness and incompleteness of gap. Complex was predominantly blue pearlescent to an observer viewing it in ambient, also suggesting a bandgap.



**Figure 2.** Diffusive transmission and reflectance graphs for PS-*block*-P4VP(DBSA)<sub>1.5</sub> indicating the formation of bandgap at ca. 460 nm.

Also the angular dependence of the mid-gap position was studied by tilting different angles ( $\theta$ ) from the normal to the sample (Figure 3). The bandgap was blue-shifted to ca. 400 nm when the angle increased from  $0^\circ$  to  $60^\circ$  (Figure 3a). It should be noted that our sample is only partly oriented and that the broadness of gap results both from variation of the long period and from a non-perfect orientation. The position of the mid-gap with different incident angles of the light is plotted in the Figure 3b (black squares). The solid line in Figure 3b illustrates calculated mid-gap position for an ideal multi-layer stack with average refractive index  $n = 1.6$  ( $\lambda(\theta) = \lambda(\theta = 0^\circ) \cdot \cos(\theta)$ ) and it coincides well with the measured values.



**Figure 3.** a) UV-Vis transmission graphs for PS-*block*-P4VP(DBSA)<sub>1.5</sub> with different incident angles of the light ( $\theta = 0 - 60^\circ$ ). b) A plot of the mid-gap position versus the incident angle of the light (black squares). Calculated mid-gap position for an ideal multi-layer stack structure with different incident angle is drawn as a solid line (the average refractive index is approximated to be ca.  $n = 1.6$ ).

## CONCLUSIONS

We have shown that PS-*block*-P4VP(DBSA)<sub>y</sub> forms hierarchically self-organized structures. The long period can be increased up to ca. 1400 Å as shown by TEM, X-ray scattering, and AFM measurements [14]. UV-Vis transmission and reflectance measurements indicate that a photonic bandgap was opened. The original bandgap was blue-shifted to ca. 400 nm when the incident angle of the light  $\theta$  was increased from  $0^\circ$  to  $60^\circ$ . The structure formation was relatively easy in such well-plasticized materials and tuning of the bandgap and the increase of refractive index difference between the domains are under investigations.

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## REFERENCES

1. J. D. Joannopoulos, R. D. Meade, and J. N. Winn, *Photonic Crystals: Molding the Flow of Light* (Princeton University Press, Princeton, 1995).
2. *Materials Science Aspects of Photonic Crystals*, MRS Bulletin, **26** (8) (2001).

3. *From Dynamics to Devices: Directed Self-Assembly of Colloidal Materials*, MRS Bulletin, **23** (10) (1998).
4. S. John and K. Busch, *J. Lightwave Technol.* **17**, 1931 (1999).
5. K. Yoshino, Y. Kawagishi, M. Ozaki, *et al.*, *Jpn. J. Appl. Phys.* **38**, L786 (1999).
6. B. Gates, S. H. Park, and Y. Xia, *Adv. Mater.* **12** (9), 653 (2000).
7. M. Müller, R. Zentel, T. Maka, *et al.*, *Chem. Mater.* **12**, 2508 (2000).
8. A. A. Zakhidov, R. H. Baughman, Z. Iqbal, *et al.*, *Science* **282**, 897 (1998).
9. Y. A. Vlasov, X.-Z. Bo, J. C. Sturm, *et al.*, *Nature* **414**, 289 (2001).
10. H. Miguez, F. Meseguer, C. López, *et al.*, *Adv. Mater.* **13** (6), 393 (2001).
11. Y. Fink, A. M. Urbas, M. G. Bawendi, *et al.*, *J. Lightwave Technol.* **17**, 1963 (1999).
12. A. Urbas, Y. Fink, and E. L. Thomas, *Macromolecules* **32**, 4748 (1999).
13. A. C. Edrington, A. M. Urbas, P. DeRege, *et al.*, *Adv. Mater.* **13** (6), 421 (2001).
14. H. Kosonen, S. Valkama, J. Ruokolainen, *et al.*, *Eur. Phys. J. E* **10**, 69 (2003).
15. I. W. Hamley, *The Physics of Block Copolymers* (Oxford University Press, Oxford, 1998).
16. J. Ruokolainen, R. Mäkinen, M. Torkkeli, *et al.*, *Science* **280**, 557 (1998).
17. J. Ruokolainen, M. Saariaho, O. Ikkala, *et al.*, *Macromolecules* **32**, 1152 (1999).
18. O. Ikkala, J. Ruokolainen, G. ten Brinke, *et al.*, *Macromolecules* **28**, 7088 (1995).