NBIT Final Report for AOARD Grant 114095

"**Tunable PhoXonic Band Gap for Self Assembly of Block Copolymers**"

December 12, 2013

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Period of Performance: 8/24/2010 – 8/24/2013

Abstract:
The collaborative efforts were aimed at designing and fabricating tunable phoXonic band gap materials by self assembly of block copolymers (BCP). We also characterized both the structures and the resultant properties and made critical comparisons with simulations. The tunable properties of stimulus-responsive materials currently attract great interest in a variety of technological applications. Photonic gels are a new class of these materials that can be tuned to reflect different wavelengths of light. Controlling this reflected color via temperature-induced and solvent-quality induced changes of self-assembled photonic materials is important for their application in sensors and as displays. We found that the thermochromic behavior of a lamellar block copolymer poly(styrene-*b*-2-vinylpyridine) (PS-P2VP) photonic gel originated from a temperature-induced change in the pKa of the P2VP blocks. Control was obtained through the manipulation of the solution pH. The findings of this work provide the basis for understanding and controlling the properties of thermochromic block copolymers fostering their use in technologically relevant applications.

Other stimuli can trigger responsive changes in photonic gels made from PS-P2VP, for example, by swelling/deswelling of the P2VP block with a selective solvent. When compared to isotropic swelling in chemically crosslinked homopolymer gels, the P2VP block in the lamellar PS-P2VP shows significantly lower degrees of swelling in alcohol-water co-solvents due to restrictions imposed by the glassy PS layers. The glassy layers completely constrain the lateral expansion of the P2VP gel block and the dislocation defect network that creates a network of interconnected PS layers and develops during BCP self-assembly, provides a counter force to vertical swelling as well as inhibits layer unbinding. Cross-sectional transmission electron microscopy (TEM) shows screw and edge dislocations as the two types of line defects in the BCP films, and suggests that these defects create an interconnected network of glassy PS block layers that serve as a retarding force during selective swelling. A model based on Flory-Huggins mixing and dislocation network strain energy was proposed to capture the swelling behavior of the BCP and then used to estimate the dislocation network density in the lamellar BCP. This work establishes the relationship between the reflective color of the BCP gel, the effective χ parameter of the gel block and the solvent, and the defect density of the BCP film, and demonstrates the potential utility of these photonic materials as a quick means to measure solvent quality or defect density.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
09 JAN 2014	**Final**	**25-08-2011 to 24-08-2013**

4. TITLE AND SUBTITLE
Tunable PhoXonic Band Gap Materials from Self-Assembly of Block Copolymers and Colloidal Nanocrystals (NBIT Phase II)

5a. CONTRACT NUMBER
FA23861114095

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Edwin Thomas

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Rice University,PO Box 1892,Houston,TX,77251-1892

8. PERFORMING ORGANIZATION REPORT NUMBER
N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AOARD, UNIT 45002, APO, AP, 96338-5002

10. SPONSOR/MONITOR'S ACRONYM(S)
AOARD

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AOARD-114095

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The collaborative efforts were aimed at designing and fabricating tunable phoXonic band gap materials by self assembly of block copolymers (BCP). We also characterized both the structures and the resultant properties and made critical comparisons with simulations. The tunable properties of stimulus-responsive materials currently attract great interest in a variety of technological applications. Photonic gels are a new class of these materials that can be tuned to reflect different wavelengths of light. Controlling this reflected color via temperature-induced and solvent-quality induced changes of self-assembled photonic materials is important for their application in sensors and as displays. We found that the thermochromic behavior of a lamellar block copolymer poly(styrene-b-2-vinylpyridine) (PS-P2VP) photonic gel originated from a temperature-induced change in the pKa of the P2VP blocks. Control was obtained through the manipulation of the solution pH. The findings of this work provide the basis for understanding and controlling the properties of thermochromic block copolymers fostering their use in technologically relevant applications.

15. SUBJECT TERMS
nano materials, nano science and technology, nano technology, Nanobiotechnology

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**Same as Report (SAR)**	**4**	

Introduction: Include a summary of specific aims of the research and describe the importance and ultimate goal of the work.
We aimed to explore the photonic responses of PS-P2VP gels to various stimuli, especially temperature changes and variations in the alcohol-water co-solvent composition.
Such responsive layered gels allow measurement of the Flory-Huggins interaction parameter between the P2VP block and the swelling solvent. Our team was ablet to use the transfer matrix model (TMM) to simulate the selective swelling in lamellar BCP films and thus to quantitatively explain the relationship between photonic responses and solvent quality.

The importance of our joint works relates to the fact that responsive photonic crystals have broad applications ranging from sensing to smart coatings. Also the Flory-Huggins parameter is an important thermodynamic parameter for polymer-solvent pairs. Moreover, to date there has been no previous report of the Flory-Huggins parameter between P2VP with binary mixtures of water and methanol, ethanol and 1-propanol at various compositions. Our work is the first model reported for lamellar BCP swelling that takes into account the presence of line defects in the films and the first quantitative model to relate the photonic gels' photonic responses to polymer-solvent interaction parameters via Flory-Rehner theory.

In summary, our overall goals were to address the future developments of responsive photonic crystals in order to benefit the fundamental understanding of the relations between photonic responses, the BCP self-assembled structure (e.g. the dislocation defects), and the polymer solution thermodynamics. Our work also demonstrates potential applications of the responsive photonic gels as sensing materials for polymer-solvent interaction parameters, co-solvent composition, or the defect density. Long term goals that our work can contribute to include sensors, smart coatings, and tunable camouflage.

Experiment: Description of the experiment(s)/theory and equipment or analyses.
Materials
A PS-P2VP diblock copolymer with a number average molecular weight of 102 kg mol^{-1} for the PS block, 97 kg mol^{-1} for the P2VP block and polydispersity of 1.12 was employed for formation of the BCP photonic gels. The BCP films were cast inside a 1 cm quartz spectrometer cuvette. A 15 □L PS–P2VP solution (5 % weight fraction in PGMEA) was spread to cover one wall of a cuvette and the film was allowed to slowly dry in air. The film was then annealed overnight in saturated chloroform vapor and allowed to dry at room temperature. The as-annealed BCP films were transparent with no reflection or scattering of visible light. The film swelled into a photonic gel when the cuvette was filled with the pure alcohols or the alcohol-water co-solvents. UV-Vis transmission spectra were collected on a Varian Cary 6000i UV-Vis-NIR spectrophotometer using the 1 cm path-length quartz cuvettes. A clean quartz cuvette was used for the baseline. The transparent dry films quickly showed color upon the addition of the co-solvent and the reflection peak positions stayed constant after several seconds. An equilibration time of 3 min was allowed at each sampling point to ensure steady-state swelling. The reflectance was calculated from the transmittance by $R = 1 - T$, assuming zero absorption or diffuse scattering. All spectral data presented in this work for a given compositional series were collected on the same film. The film was blown dry with nitrogen before swelling again. The error bars were estimated by repeatedly swelling the same sample 5 times. Due to the limit of the wavelength range of the UV-Vis spectrophotometer and the absorption by the BCP, spectra below 300 nm could not be obtained.

Homopolymer P2VP gels were synthesized from 2VP monomer. A 2 % mol DVB (purified by passing through a neutral alumina column) was added to the 2VP as a crosslinker, and the mixture was dissolved at a concentration of 40% in 1:1 ethanol-water. Uniaxial compression experiments were performed on a Zwick/Roell Z2.5/TS1S materials testing machine and TestX-pert V10.1 master software (Ulm, Germany) with a 20 N load cell. The compression modulus was calculated from the linear region between 5 % and 10 % nominal strain. Gel pieces (approximately 2 g each) were then dried in a hood and then in a vacuum oven, both at room temperature, then soaked in various alcohol-water mixtures for 3 days. The mass swelling ratios for all the various alcohol-water co-solvents were taken as the ratio of the swollen gel weight and the dry P2VP network weight.

Results and Discussion: Describe significant experimental and/or theoretical research advances or findings and their significance to the field and what work may be performed in the future as a follow on project. Fellow researchers will be interested to know what impact this research has on your particular field of science.

Our results suggest that the photonic gel's responsive behavior depends on the detailed defect content of the film. For example, when we make a very perfect film, the swelling is very slow or there is essentially no swelling, whereas a film that appears slightly hazy even when dry (indicating defects and layer misalignment that create some light scattering) swells rapidly to various extent depending not only on solvent, pH, temperature etc but also on the particular defect content of the particular film. The Thomas and Kang groups collaborated by using the sol - gel infill technique developed by the Kang group back in 2009 to view the cross section of the films for various types of defects. An SEM figure from the Kang 2012 paper shows the internal structure as a function of degree of swelling. Such images allow a direct means to evaluate the number density and type of defects in the layers. In particular, the thin PS layers could be monitored to see how they are interconnected via defects such as screw dislocations running perpendicular to the layers. Ref; Kang, C.; Kim, E.; Baek, H.; Hwang, K.; Kwak, D.; Kang, Y.; Thomas E. L. "Full Color Stop Bands in Hybrid Organic/Inorganic Block Copolymer Photonic Gels by Swelling-Freezing" *J. Am. Chem. Soc.* **2009**, *131*, 7538-7539.

In the future, advances in processing may afford the opportunity to make defect-free films and then purposefully create a set of known pinning sites (for example, by irradiation with an electron beam so as to locally crosslink the film) so as to controllably alter the swelling kinetics. Both the swelling rate and the long time, equilibrium color (degree of swelling) are of interest. Intentionally placed pores (via incorporation and later dissolution of insoluble salts or use of focused laser beams to created patterned hole arrays) will provide for faster solvent transport and color response in sensor applications. Our hypothesis is that regions with more defects swell faster but the final degree of swelling would be somewhat less as already observed in the real-time spectra and some cross-sectional SEM images. Developing simple models ("3D honeycomb") for equilibrium swelling versus the average defect-defect correlation distance would be useful. One should be able to locate different regions on the same sample exhibiting different colors, label them and do cross sectional AFM/SEM to find out if the defect structures are different, confirming that the defects are aiding solvent transport into the system, thus speeding the kinetics but at the same time, defects are pinning the glassy layers, thus limiting the extent of swelling. It should be possible to also extend the swelling model to polyelectrolyte gels by studying the quaternized PS-QP2VP gels. With significant effort at confocal microscopy or cross sectional TEM, the

statistical analysis of the set of dislocations in lamellar BCP films and the relationship to processing conditions (film casting, solvent vapor annealing) could be better established. Of course, the effect of the BCP molecular weight on the swelling and the BCP chemistry on on selective swelling could also be usefully explored.

It may be possible to use a block copolymer based system as a smart window coating to reflect IR radiation only in hot weather. The idea is to use a temperature-dependent solvent partitioning between the two blocks to control the swelling ratio such that at higher temperatures the colored film (visible reflection of light in the visible region) is replaced by a clear film that allows the visible light to strike a white reflective substrate as well as to reflect that IR components of the incident radiation, thus preventing solar heating.

List of Publications and Significant Collaborations that resulted from your AOARD supported project: In standard format showing authors, title, journal, issue, pages, and date, for each category list the following:

a) papers published in peer-reviewed journals

Kim, E., Kang, C., Baek, H., Hwang, K., Kwak, D., Lee, E., Kang, Y., Thomas, E.L., "Control of Optical Hysteresis in Block Copolymer Photonic Gels: A Step Towards W et Photonic Memory Films," *Advanced Functional Materials*, 20 (11), 1728-1732 (2010).

Hwang, K. Kwak, D. Kang, C. Kim, D., Ahn, Y., Kang, Y. "Electrically Tuna ble Hysteretic Photonic Gels for Nonvolatile Display Pixels," *Angew. Chem. Int. Ed.* 2011, 50, 6311-6314

Ahn, Y.; Kim, E.; Hyon, J.; Kang, C.; Kang, Y., ."Photoresponsive Block Cop olymer Photonic Gels with Widely Tunable Photosensitivity by Counter-Ions". *Advanced Materials*, Volume 24, issue 23 (June 19, 2012), p. OP127-OP130. ISSN: 0935-9648 DOI: 10.1002/adma.201103767

Lee, J-H., Koh, C.H., Singer, J., Jeon, S-J., Maldovan, M., Stein, O., Thomas, E.L., "Ordered Polymer Structures for the Engineering of Photons and Phonons", *Advanced Materials*, 12 DEC 2013 DOI: 10.1002/adma.201303456