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Optically Pumped Surface-Emitting Lasing Using Self-Assembled Block-Copolymer-Distributed Bragg Reflectors

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ABSTRACT

A thin-film organic laser cavity using a block-copolymer-based one-dimensional (1D) photonic crystal was fabricated. Polymeric distributed Bragg reflectors (DBRs) were prepared through the self-assembly of a lamellar-forming poly(styrene-*b*-isoprene) (PS-*b*-PI) diblock copolymer having a 1D photonic stop band overlapping with the fluorescence spectrum of a gain medium. Optically pumped surface-emitting lasing was obtained using poly(methyl methacrylate) (PMMA) doped with 1,4-di-(2-methylstyryl)benzene (Bis-MSB) as an organic gain medium and the polymeric self-assembled DBR as a spectral-band selective feedback element.

Over the past few years, block copolymers have been considered as a unique materials platform for fabricating large-area well-ordered photonic band-gap structures.[1] Block copolymers microphase-separate into periodic microdomains on the length scale of the blocks driven by a competition between a tendency to reduce the interfacial free energy and to increase the conformational entropy of the constituting polymer chains.[2,3] With an appropriate microdomain size (d_i) that is large enough to interact with visible light ($d_i \approx \lambda/4n_i$, where n_i is the refractive index of the respective microdomain and λ is the wavelength of light in vacuum), block copolymers can create periodic dielectric structures having a photonic stop band in the optical frequency range. Various block copolymer systems, such as lamellar, cylindrical, and double-gyroid diblock copolymers,[4−7] blends of diblock copolymer with homopolymers or plasticizers,[8,9] and block copolymer nanocomposites doped with inorganic nanoparticles, or liquid crystals,[10−12] were successfully used to prepare 1D, 2D, and 3D visible wavelength photonic crystals.

Although the basic concept of self-assembled block-copolymer-based photonic band-gap materials as *passive* photonic structures has been well-demonstrated, little work has been done in terms of realizing *active* photonic devices using these materials. Though the performance of block-copolymer-based photonic structures is somewhat limited by the relatively low dielectric contrast and intrinsic defect formation during self-assembly, these materials could be employed where precision performance is not required because they offer many advantages, such as a range of easily accessible periodic structures, lightweight, mechanical flexibility, and low-cost processing over a large area. One potential application of such self-assembled polymeric photonic crystals is to use them as resonators in a photonic microcavity to provide spectrally selective feedback for lasing.[13−16] Here we illustrate that thin films of a high-molecular-weight lamellar-forming poly(styrene-*b*-isoprene) (PS-*b*-PI) block copolymer can be utilized to produce self-assembled distributed Bragg reflectors, which can act as a narrow spectral-band selective element for defining a photonic microcavity. Optically pumped surface-emitting lasing has been demonstrated with fluorescent organic laser dyes in a polymer matrix as a gain medium deposited between block-copolymer-based Bragg reflectors.

The high-molecular-weight photonic PS-*b*-PI block copolymer was synthesized via anionic polymerization with sequential addition of styrene and isoprene monomer in cyclohexane/benzene mixed solvent.[17] The molecular weight and composition of the block copolymer are 5.90×10^5 g/mol (PDI: 1.09), 54/46 (PS/PI, wt/wt) as measured by gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) analysis. Figure 1 shows a bright-field transmission electron microscopy (TEM) micrograph from the cryomicrotomed sample of the PS-*b*-PI block copolymer

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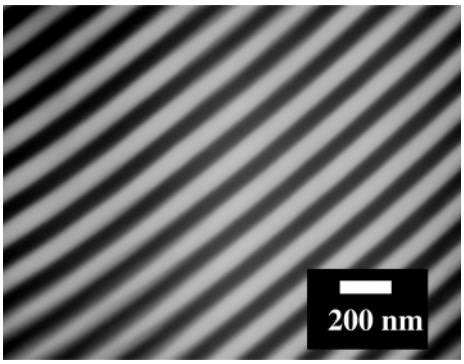

Figure 1. Bright-field TEM micrograph of cryomicrotomed PS-*b*-PI block copolymer showing a 1D periodic lamellar morphology, in which the dark regions correspond to PI domains preferentially stained with OsO_4 and the bright regions correspond to PS domains. The domain periodicity is approximately 140 nm (PS, 76 nm; PI, 64 nm).

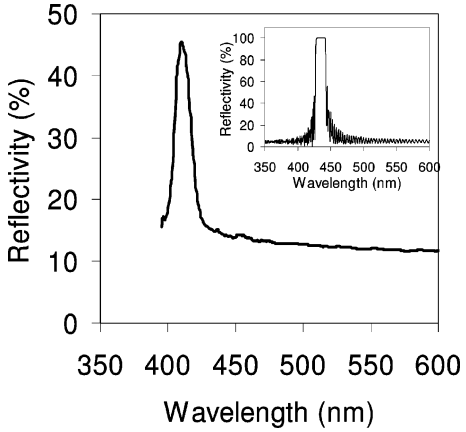

Figure 2. Experimental reflectivity spectrum of the fabricated block-copolymer-based distributed Bragg reflector at near-normal incidence using a reflection-mode optical microscope connected to a fiber-optic spectrometer. The inset shows a calculated reflectivity spectrum using the transfer matrix method at a normal incidence for a finite 1D periodic structure, assuming 300 layers of PS (76 nm, $n = 1.59$) and PI domains (64 nm, $n = 1.51$).

exhibiting the 1D periodic lamellar morphology, in which the dark regions correspond to the PI domains preferentially stained with osmium tetroxide (OsO_4) and the bright regions correspond to the PS domains. The domain periodicity from the TEM micrograph is approximately 140 nm (PS, 76 nm; PI, 64 nm).

The resulting 1D periodic dielectric structure selectively reflects light of a range of frequencies due to a constructive interference at the set of interfaces between high (PS, $n = 1.59$) and low (PI, $n = 1.51$) refractive index domains. Figure 2 shows the experimentally measured reflectivity spectrum of the self-assembled distributed Bragg reflector at near-normal incidence of light, in which the peak reflectivity occurs at 410 nm and the width of the stop band (the full width at half-maximum: fwhm) is about 14 nm.

This reflectivity spectrum was obtained using an optical microscope (Zeiss Axioscop) equipped with a fiber-optic spectrometer (Stellarnet EPP2000) using a silver-coated metallic mirror as a 100% reference. Because of the numerical aperture of the objective lens (Carl Zeiss, Neo-

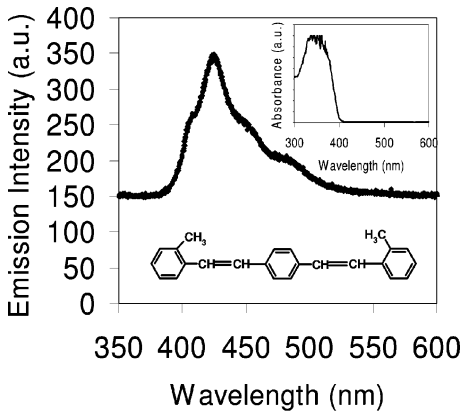

Figure 3. Photoluminescence (PL) spectrum from a solid film of Bis-MSB (0.1 wt %, 355 nm excitation) in PMMA. The fwhm of the PL spectrum is about 41 nm. The inset shows the absorption spectrum from the same sample, where the absorption maximum is located at around 350 nm.

Fluora 10X, N. A. = 0.3), the spectrum is not from a pure normal incidence reflectance but represents a convolution of multiple reflectance spectra over the incidence angles of 0° to ~17.5°. The inset in Figure 2 shows a calculated reflectivity spectrum at a normal incidence of light by transfer matrix method[18] for a finite 1D periodic structure assuming 300 layers of PS (76 nm, $n = 1.59$) and PI domains (64 nm, $n = 1.51$), for which the fwhm is 18 nm and the band-gap center is located at 435 nm. The relatively narrow experimental reflectivity band (fwhm ≈ 14 nm) of the sample suggests that the effective dielectric contrast between PS and PI domains is reduced due to the effect of some retained solvent (cumene: $n \approx 1.49$). The narrow bandwidth also indicates that the parallel alignment of the lamellar microdomain orientation is quite good due to the influence of the substrate. Given the measured peak wavelength position (410 nm) and the width (fwhm: 14 nm) of the reflectivity band, we can estimate the solvent concentration to be approximately 10 wt % by assuming a parallel orientation of lamellae, a uniform distribution of solvent in PS and PI domains (i.e., neutral solvent), and a constant ratio of PS and PI domain thicknesses (i.e., $d_{PS}/d_{PI} = 76/64$ as obtained from TEM). The spectral response of this block-copolymer-based distributed Bragg reflector can be readily tuned by simply controlling the solvent concentration in the block copolymer solution, which can affect the spacings and the effective refractive indices of the respective microdomains.[19]

For the gain medium, an organic chromophore, (1,4-di-(2-methylstyryl)benzene (Bis-MSB, Exciton) was dissolved in PMMA at a concentration of 0.1 wt % (to PMMA) using tetrahydrofuran (THF) as the solvent. Figure 3 is the photoluminescence spectrum from a solid film (thickness ≈ 1 mm) of Bis-MSB in PMMA cast on a glass substrate excited by a 355 nm pulse, in which the peak fluorescence occurs at 425 nm and the fwhm is 41 nm. The inset in Figure 3 shows the absorption spectrum from the same sample obtained on a Hewlett-Packard 8453 diode array spectrophotometer, where the absorption maximum is around 350 nm.

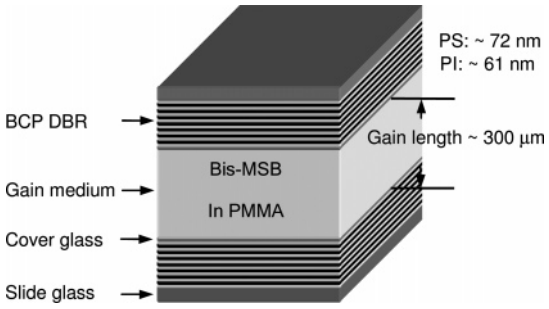

Figure 4. Schematic of the block-copolymer-based laser cavity, composed of a gain medium, Bis-MSB and PMMA, enclosed between two block-copolymer-based distributed Bragg reflectors. The thicknesses of PS and PI domains are estimated values at 10 wt % solvent concentration based on the peak position and fwhm of the reflectivity spectrum.[19]

A thin-film organic laser cavity was fabricated by sandwiching the gain medium between two block-copolymer-based reflectors as shown schematically in Figure 4. First, the self-assembled reflectors were prepared from the solvent containing PS-*b*-PI cast between a microscope slide glass and a cover glass (film thickness $\approx 50\ \mu$m). After measuring the reflectivity data from the reflectors, the gain medium of PMMA/Bis-MSB in THF was then incorporated between the two reflectors with a thickness of about 300 μm using a spacer. On the basis of a simple order-of-magnitude cavity analysis with the known gain length ($L = 300\ \mu$m) and experimentally measured reflectivity of the block-copolymer-distributed Bragg reflector ($R_1 = R_2 \approx 0.48$), we can estimate the threshold gain coefficient required for lasing, which is about 24.5 cm^{-1} (Supporting Information). Although the exact optical gain coefficient of the gain medium (Bis-MSB in PMMA) in our laser system was not measured in this study, this estimated threshold gain coefficient is in a reasonable range that can be achieved with typical organic dyes.[20,21]

The experimental setup for the lasing experiment conducted at room temperature is shown in Figure 5. A frequency-tripled output of a Q-switched Nd:YAG laser (Continuum NY 60B, $\lambda = 355$ nm, pulse width = 10 ns, repetition rate = 20 Hz) was used as an excitation source. The pump laser beam was focused onto the sample with a 2.5-cm-diameter lens of 20 cm focal length and at an incidence angle of 30° from the normal to the sample surface, giving a beam diameter at the sample of about 300 μm. As the average power of the excitation pulse increased above the lasing threshold, a well-defined lasing beam was vertically emitted from the surface of the sample in both the forward and backward directions. The backward emitted light was collected using a fiber-optic spectrometer (Ocean Optics HR 2000), and a set of neutral density filters were used to control the average power of the excitation pulses.

Figure 6 shows a highly directional stimulated emission from the sample surface at a pump power greater than the lasing threshold, which is clear evidence for lasing. The corresponding emission spectra were recorded at various excitation pump powers as shown in Figure 7. Above the lasing threshold, a sharp lasing peak occurs at around 410

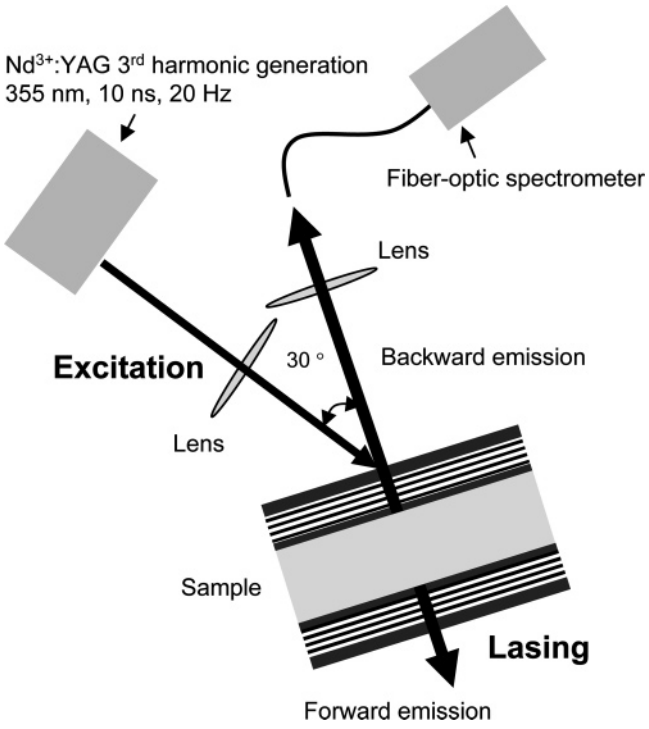

Figure 5. Schematic of the experimental setup for measuring the lasing output from the BCP/gain/BCP device.

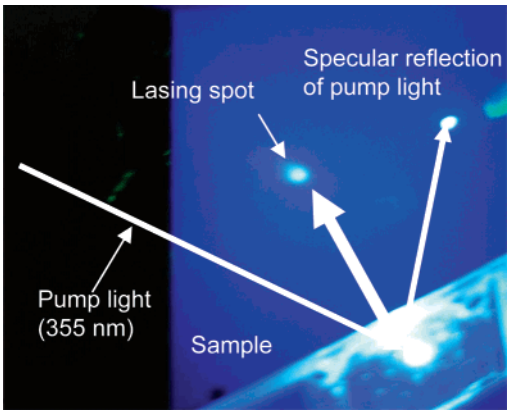

Figure 6. Photograph of the 410 nm lasing from the block-copolymer-based laser structure. A highly directional lasing output in the backward direction was observed on a white background.

nm with a significant spectral narrowing (fwhm ≈ 1.0 nm, which is limited by a spectral resolution of our experimental setup). To further confirm lasing activity, we obtained the pump power dependence of the emission intensity at the lasing wavelength as shown in the inset of Figure 7. Under the experimental conditions of this study, the lasing threshold was around 280 mJ/cm^2 (0.2 mJ/pulse on the area of 300 μm diameter). Figure 8 shows a lasing spectrum with the same gain medium (Bis-MSB in PMMA) but obtained from a cavity sandwiched between an aluminum-coated mirror and a glass slide using the same pump configuration as that in Figure 5. In this arrangement, the metallic mirror and the glass slide do not provide any spectrally selective feedback. The lasing thus occurs at 425 nm where the dye emission is maximum (Figure 3) and the fwhm is 4 nm. This result further confirms that the narrow spectral selectivity of the

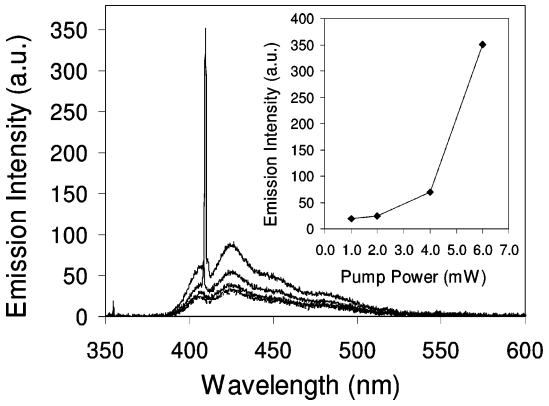

Figure 7. Emission spectra obtained at various pump powers. The fwhm of the lasing peak is 1 nm. The inset shows the emission intensity at the lasing wavelength (410 nm) as a function of pump power, which clearly shows a threshold for lasing at around 4 mW pump power (0.2 mJ pulse energy).

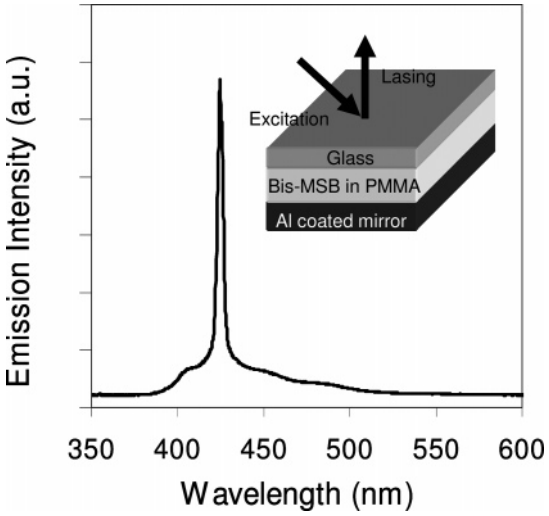

Figure 8. Lasing spectrum from a solid film of Bis-MSB (0.1 wt %) in PMMA sandwiched between an aluminum-coated mirror and a glass slide pumped by a 355 nm pulse laser, where the lasing peak occurs at 425 nm and the FWHM is 4 nm. The inset shows a schematic of the sample.

lasing output obtained from the block copolymer laser cavity results from the selective feedback of block-copolymer-based distributed Bragg reflectors.

In summary, we have utilized thin films of a high-molecular-weight PS-*b*-PI block copolymer as a narrow spectral-band selective feedback element for constructing a laser cavity. With fluorescent organic laser dyes in a PMMA polymer matrix as a gain medium, optically pumped surface-emitting lasing action has been demonstrated. This block-copolymer-based photonic structure opens the possibility of creating all-organic, flexible, and self-assembled laser devices with fast and low-cost processing. Further studies regarding stimulus-responsive tunable block-copolymer photonic crystals with various parameters such as solvent (solvatochromic), temperature (thermochromic), mechanical strain (mechanochromic), and electric field (electrochromic) are currently under investigation, and their applications for lasing, sensing, and display are quite promising.

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Supporting Information Available: Estimation of threshold gain coefficient for lasing. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Yoon, J.; Lee, W.; Thomas, E. L. *MRS Bull.* **2005**, *30*, 721−726.
(2) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525−557.
(3) Thomas, E. L.; Lescanec, R. L. *Philos. Trans. R. Soc. London, Ser. A* **1994**, *348*, 149−166.
(4) Urbas, A.; Fink, Y.; Thomas, E. L. *Macromolecules* **1999**, *32*, 4748−4750.
(5) Deng, T.; Chen, C.; Honeker, C.; Thomas, E. L. *Polymer* **2003**, *44*, 6549−6553.
(6) Urbas, A. M.; Maldovan, M.; DeRege, P.; Thomas, E. L. *Adv. Mater.* **2002**, *14*, 1850−1853.
(7) Yoon, J.; Mathers, R. T.; Coates, G. W.; Thomas, E. L. *Macromolecules* **2006**, *39*, 1913−1919.
(8) Urbas, A.; Sharp, R.; Fink, Y.; Thomas, E. L.; Xenidou, M.; Fetters, L. J. *Adv. Mater.* **2000**, *12*, 812−814.
(9) Osuji, C.; Chao, C. Y.; Bita, I.; Ober, C. K.; Thomas, E. L. *Adv. Func. Mater.* **2002**, *12*, 753−758.
(10) Bockstaller, M.; Kolb, R.; Thomas, E. L. *Adv. Mater.* **2001**, *13*, 1783−1786.
(11) Fink, Y.; Urbas, A. M.; Bawendi, M. G.; Joannopoulos, J. D.; Thomas, E. L. *J. Lightwave Technol.* **1999**, *17*, 1963−1969.
(12) Valkama, S.; Kosonen, H.; Ruokolainen, J.; Haatainen, T.; Torkkeli, M.; Serimaa, R.; Ten Brinke, G.; Ikkala, O. *Nat. Mater.* **2004**, *3*, 872−876.
(13) Jakubiak, R.; Bunning, T. J.; Vaia, R. A.; Natarajan, L. V.; Tondiglia, V. P. *Adv. Mater.* **2003**, *15*, 241−244.
(14) Finkelmann, H.; Kim, S. T.; Munoz, A.; Palffy-Muhoray, P.; Taheri, B. *Adv. Mater.* **2001**, *13*, 1069−1072.
(15) Lawrence, J. R.; Ying, Y. R.; Jiang, P.; Foulger, S. H. *Adv. Mater.* **2006**, *18*, 300−303.
(16) Yang, P. D.; Wirnsberger, G.; Huang, H. C.; Cordero, S. R.; McGehee, M. D.; Scott, B.; Deng, T.; Whitesides, G. M.; Chmelka, B. F.; Buratto, S. K.; Stucky, G. D. *Science* **2000**, *287*, 465−467.
(17) Ndoni, S.; Papadakis, C. M.; Bates, F. S.; Almdal, K. *Rev. Sci. Instrum.* **1995**, *66*, 1090−1095.
(18) Born, M.; Wolf, E. *Principle of Optics, 7th ed.*; Cambridge University Press: Cambridge, 1999.
(19) Yoon, J. Block Copolymer Photonic Crystals: Towards Self-Assembled Active Optical Elements. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, 2006.
(20) Dienes, A. *Appl. Phys.* **1975**, *7*, 135−139.
(21) Itoh, U.; Takakusa, M.; Moriya, T.; Saito, S. *Jpn. J. Appl. Phys.* **1977**, *16*, 1059−1060.

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