

Conjugated polymers as solid-state laser materials

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Abstract

A brief review of the recent emergence of semiconducting π -conjugated polymers as solid-state laser materials is given. Photopumped gain narrowing and lasing in undiluted submicron thick polymer films have been demonstrated. The dramatic collapse of the emission linewidth (to as little as 7 nm) occurs at very low pump-energy thresholds. Gain narrowing is found in over a dozen different polymers representing a variety of molecular structures and is explained in terms of amplified spontaneous emission (ASE) in planar waveguides, which allows the distance traveled by emitted photons to exceed the short intrinsic gain lengths. Prospects for producing electrically pumped solid-state polymer diode lasers using this class of materials are discussed in the context of the low-threshold gain narrowing in submicron-thick films. © 1997 Elsevier Science S.A.

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1. Introduction

The dream of using semiconducting polymers in high-performance 'plastic' photonic devices is rapidly becoming reality. Notably absent from the list of semiconducting polymer devices, however, is the polymer laser diode. As the first important step in exploring the feasibility of such laser diodes, optically pumped stimulated emission, gain, and lasing have recently been observed in over a dozen different semiconducting polymers representing a variety of molecular structures with emission wavelengths spanning the visible spectrum.

Many conjugated polymers are luminescent materials with a Stokes shift which separates emission sufficiently far from the absorption edge that self absorption is minimal. Because of the large joint density of states associated with the direct π to π^* transition of these quasi-one-dimensional semiconducting polymers, the absorption coefficient (α) is large, typically $\alpha \approx 10^5 \text{ cm}^{-1}$ or greater [1]. To first order, the cross section for stimulated emission (SE) is the same as that for absorption, so the gain length should be essentially equal to the absorption length scaled by the fraction of chromophores in the excited state. Therefore, an inverted population can be achieved by pumping the π to π^* transition; this does not simultaneously stimulate emission because the absorption

and emission are spectrally separated. Thus, semiconducting luminescent polymers offer promise as novel laser materials with gain lengths in the micron regime.

Although laser dye molecules also have a Stokes shift which facilitates population inversion, an important distinction between such dyes and conjugated polymers is that the former undergo concentration quenching. In polymers, there is no limit to the concentration; neat, undiluted, solid films with photoluminescence (PL) quantum efficiencies as high as 70% are available with a correspondingly high cross section for SE. This is a significant advantage over laser dyes, which must be diluted to optimal concentrations, and which therefore have inherently lower gain.

Interest in using semiconducting polymers as solid-state laser materials was initiated by the demonstration of gain narrowing in dilute blends of MEH-PPV in polystyrene containing a dispersion of TiO_2 nanoparticles [2]. Photopumped gain narrowing was subsequently reported for submicron-thick films, neat and undiluted, of over a dozen soluble conjugated polymers in planar waveguide structures [3,4]. Moreover, lasing has been observed in microcavities from PPV [5] and a soluble PPV derivative, BuEH-PPV (see Fig. 1) [6]. New polymers have been developed that also show spectral narrowing above threshold in solutions [7,8] and in the solid state [9,10].

Achievement of gain narrowing requires that two criteria be fulfilled:

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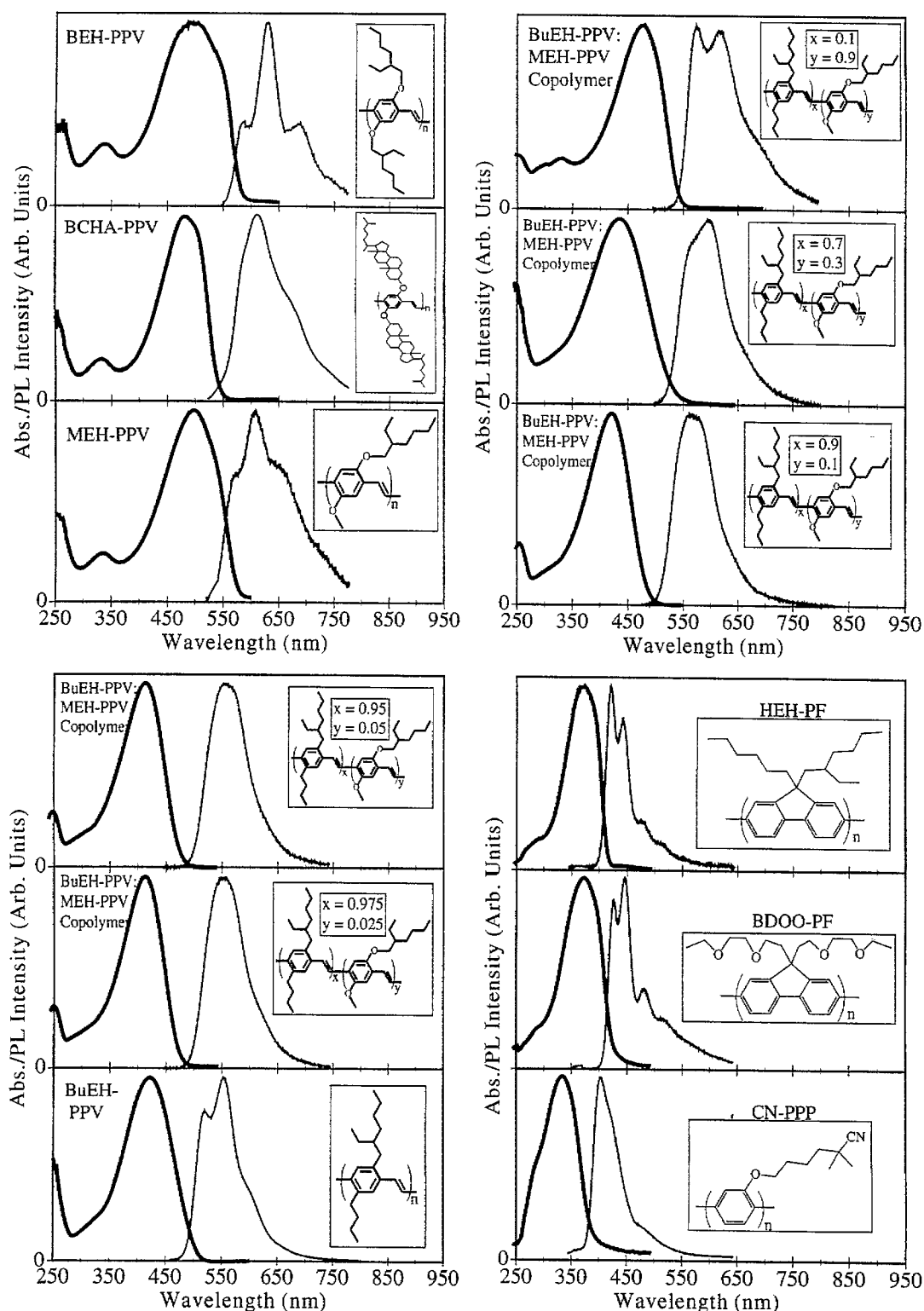


Fig. 1. Absorption (heavy smooth curves) and photoluminescence (thin, slightly noisy curves) spectra of neat thin films of BuEH-PPV, BCHA-PPV, MEH-PPV, BEH-PPV, BuEH-PPV/MEH-PPV copolymers at different monomer ratios, HEH-PF, BDOO-PF, CN-PPP. Insets: molecular structures.

1. The active polymer medium must exhibit SE. Many semiconducting polymers fall into this class and are suitable as the active medium for plastic lasers (Fig. 1).
2. Some type of resonant structure must enable the emitted photons to travel a distance greater than the gain length in

the excited polymer. Optical feedback in polymer lasers has been provided by microcavities and planar waveguides with distributed feedback [11].

Light amplification by the SE process in the absence of resonant feedback can be placed in two categories [12]:

cooperative processes, where the dipoles are coupled together through their overlapping radiation fields, can be either *superradiance* (SR) or *superfluorescence* (SF). For SR, the dipoles are initially coherently prepared, while for SF they are initially uncorrelated, although they evolve into a coherent emission after a certain delay time. In *collective* processes, such as amplified SE (ASE), the spontaneous emission coming from a distribution of emitters is linearly amplified by the gain medium. Although there is general agreement among the recent experimental observations of spectral narrowing in conjugated polymers, a variety of explanations have been proposed, including ASE in asymmetric waveguides [3], lasing in microcavities [5,6], cooperative phenomena such as superradiance or superfluorescence [13], and emission from condensed excitons [14]. Some of these possibilities are considered further below.

2. Experimental

Sample preparation procedures and instrumentation for gain-narrowing experiments using thin-solid-film waveguides have been described in detail elsewhere [3]. DCM dye, poly(*N*-vinyl carbazole) (PVK), and ITO glass were commercially available. Waveguides consisted of simple layered structures: glass/polymer/air and glass/ITO/PVK/BuEH-PPV/air. Polymer films were prepared in nitrogen atmosphere by spin-casting from solution (anhydrous tetrahydrofuran, *p*-xylene, or chlorobenzene) and film thicknesses were measured with a Dektak profilometer. The films were stored in an inert environment until immediately before use in the optical characterization experiments, which were carried out under ambient conditions. The refractive indices (n) of the films were determined from modal waveguide characterization by the prism coupling technique [15]. Glass microscope slides were used as substrates for most of the experiments.

Light emission was typically collected from the front face of the sample, but gain-narrowed emission could be detected in all directions partly as a result of scattering by imperfections in the film. The excitation source was a 10 Hz, Q -switched Nd:YAG laser which provided ~ 10 ns pulses at 532 and 355 nm focused to a ~ 1 mm diameter spot. The first anti-Stokes Raman line (435 nm) from a high-pressure H_2 cell pumped at 532 nm was also used. The energy per pulse was controlled with calibrated neutral-density filters.

3. Gain narrowing in semiconducting polymers

The luminescent conjugated polymers used in this work are functionalized PPV, PPP, and PF derivatives with emission spanning nearly the entire visible spectrum. Although gain narrowing has been observed in all of the polymers shown in Fig. 1, these materials have thin-film PL efficiencies which differ markedly. Some of the thin-film PL quantum

yields are: BuEH-PPV (0.62), BCHA-PPV (0.53), BEH-PPV (0.13), MEH-PPV (0.21), and CN-PPP (0.46).

The basic data set which demonstrates gain narrowing in conjugated polymers is presented in Fig. 2. The evolution of the PL spectrum is shown as a function of the pump pulse energy for three representative polymers. In all cases, as the pump energy is increased, a line-narrowed peak rises out of the broad emission spectrum, until at sufficiently high energies (equal to or greater than a few microjoules per pulse), only the line-narrowed peak survives, and the broad wings of the PL are relatively suppressed. The existence of gain in neat, undiluted films of BuEH-PPV under photoexcitation has been confirmed directly [16]; this clearly indicates that the dramatic collapse of the linewidth (from 130 to 8.5 nm) at very low pumping energies (~ 1 μ J) for neat films of BuEH-PPV is due to gain narrowing. Fig. 3, which shows the PL linewidth as a function of the energy of the pump pulse, demonstrates a well-defined pump-energy threshold for line narrowing, a signature expected for the gain associated with ASE.

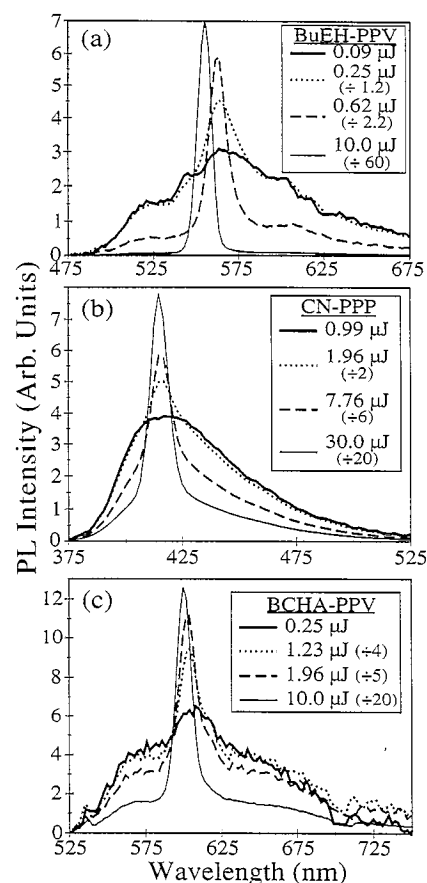


Fig. 2. Photoluminescence spectra at different excitation energies for neat films of different conjugated polymers spin cast on glass. (a) A 210 nm thick film of BuEH-PPV pumped at 435 nm. (b) A 100 nm thick film of CN-PPP pumped at 355 nm. (c) A 580 nm thick BCHA-PPV film, pumped at 532 nm. For all three polymers, the thick solid curves show the PL for a pump energy below the gain-narrowing threshold, the dotted and dashed curves for pump energies just slightly below and above threshold, respectively, and the thin solid curves for pump energies above threshold.

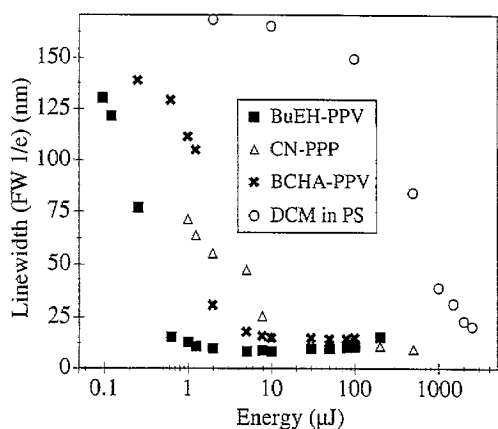


Fig. 3. Emission linewidth (full width at $1/e$ height) as a function of pump pulse energy (on a log scale) for the same polymer films used in Fig. 2. Solid squares, 210 nm thick film of BuEH-PPV pumped at 435 nm; open triangles, 100 nm thick film of CN-PPP pumped at 355 nm; heavy crosses, 580 nm thick film of BCHA-PPV pumped at 532 nm; open circles, a 2.6 wt.% film of DCM laser dye in PS of 3600 nm thickness pumped at 532 nm with comparable optical density to the BuEH-PPV film.

An important feature evident in Fig. 2 is the blue shift of the emission peak at higher excitation energies. This blue shift occurs at the same energy as the threshold for gain narrowing, suggesting that SE occurs on a time scale comparable to or faster than interchain energy migration [2], and providing another direct signature of optical gain. The other polymers that were investigated also exhibit the same type of gain-narrowing behavior (Fig. 1). The energy thresholds for narrowing, the pump wavelengths used, the PL emission maxima, and the final narrowed linewidths for all the polymers studied are summarized in Ref. [3].

If the gain lengths are indeed in the micron regime, the energy threshold for gain narrowing should be substantially lower than for conventional laser materials. For reference, therefore, thin films of various concentrations of the laser dye DCM suspended in polystyrene (PS) were also tested (see Fig. 3). DCM was diluted to an optimal concentration (2.6%) in PS to minimize concentration quenching. The thickness of these films was adjusted to provide optical densities comparable to those of the BuEH-PPV films discussed in Figs. 2 and 3 above. Although these films have DCM concentrations nearly two orders of magnitude higher than in a typical dye laser [17], the threshold for gain narrowing is still over 1000 times higher than that of BuEH-PPV. Thus, conjugated polymers emerge as a unique class of laser materials: they provide the intense absorption and emission characteristics of organic dyes, but with the substantial advantage of having a much higher density of chromophores in the solid state. The higher density of chromophores results in significantly shorter gain lengths and therefore, lower energy thresholds for gain narrowing.

4. Amplified spontaneous emission (ASE) in planar waveguides

The refractive indices (n) at the emission wavelengths for all the polymers studied are in the range $1.56 \leq n_{\text{polymer}} \leq 2.0$;

i.e., larger than those of the surrounding media ($n_{\text{glass}} = 1.52$, $n_{\text{air}} = 1.0$) in thin-film samples. Therefore, neat polymer films cast over glass substrates constitute asymmetric planar waveguides. For an asymmetric waveguide, a cutoff film thickness (h_{cutoff}) exists, below which the fundamental mode cannot propagate [15]. This cutoff thickness is dependent on the refractive indices of the cladding (air), film, and substrate. Based on the refractive indices of the polymer films as determined by modal waveguide characterization at 633 nm, the calculated h_{cutoff} values are 120 and 200 nm for BuEH-PPV and BCHA-PPV films on glass, respectively. Light could not be coupled into the MEH-PPV waveguide and therefore the refractive index of MEH-PPV is estimated to be comparable to or greater than that of the prism coupler ($n \sim 1.8$).

The dependence of gain narrowing on film thickness was studied experimentally for neat films of three conjugated polymers, BuEH-PPV, BCHA-PPV, and MEH-PPV, as well as for the reference films of DCM in PS. To demonstrate the effects of thickness on the gain-narrowing behavior, we plot the high-energy ($\geq 10 \mu\text{J}$) PL linewidth as a function of the film thickness for each of these three polymers in Fig. 4. A well-defined cutoff thickness for the presence of gain narrowing is evident at 116 ± 10 nm for BuEH-PPV, 215 ± 30 nm for BCHA-PPV, and 70 ± 15 nm for MEH-PPV. Thus, for both BuEH-PPV and BCHA-PPV, the experimentally observed cutoff thicknesses are in excellent agreement with the calculated waveguide cutoff values. For MEH-PPV, the calculated refractive index based on the experimentally determined cutoff thickness is in the range 1.8 to 2.0, which is consistent with the estimate mentioned above. The observed cutoff thickness for the DCM-PS films leads to a calculated n between 1.56 and 1.59, in agreement with handbook values for the index of refraction of pure PS. Since the coupling among the emissive dipoles in the polymer film could not be altered by merely turning the waveguiding on or off, the possibility of superfluorescent emission as the sole mechanism of gain narrowing is eliminated.

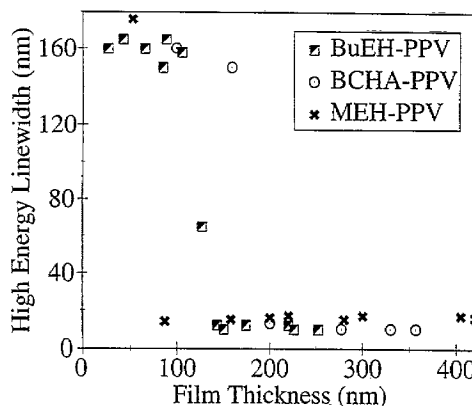


Fig. 4. Linewidth of the PL spectrum at a high pump energy (≥ 10 mJ per pulse) as a function of the film thickness for BuEH-PPV (half-filled squares, 435 nm excitation), BCHA-PPV (dotted circles, 532 nm excitation) and MEH-PPV (heavy crosses, 532 nm excitation) films spin-cast from THF on glass substrates.

5. Role of cladding layer in planar waveguides

Electrically pumped laser diodes would require carrier-injecting electrodes, such as ITO and metals, in the vicinity of the conjugated polymer. Because the PL is quenched within a few hundred angstroms of metal surfaces [18], the electrodes might complicate the development of polymer laser diodes. Although ITO suppresses the waveguiding, insertion of a layer of PVK between the PL polymer and the ITO restores the waveguiding and the gain narrowing.

Results from BuEH-PPV films on glass, with and without ITO as well as with PVK cladding layers of two different thicknesses, are presented in Fig. 5. The ITO electrode suppresses gain narrowing by preventing the formation of a planar waveguide in the active medium. Because of the high index of refraction of ITO ($1.8 \leq n_{\text{ITO}} \leq 2.1$) [19], a guided mode cannot be supported in a BuEH-PPV film on ITO at the gain wavelength (≈ 550 nm) ($n_{\text{BuEH-PPV}} = 1.78$ at 550 nm [11]). Waveguiding can be restored by inserting a PVK cladding layer ($n_{\text{PVK}} = 1.68$ at 568 nm) of appropriate thickness, a promising result for LEDs which often show higher EL efficiency when PVK is used as a hole-transport layer. The light can then be guided in the BuEH-PPV layer, although it penetrates into the PVK layer, leading to an increase in the threshold with respect to BuEH-PPV on glass, as observed.

The conducting ITO also reduces η_{PL} of the polymer film; we note, however, that polymers with η_{PL} substantially lower than that of BuEH-PPV, such as MEH-PPV ($\eta_{\text{PL}} \approx 15\%$) [18], exhibit gain narrowing in waveguides. Thus, for BuEH-PPV with $\eta_{\text{PL}} \approx 62\%$, PL quenching by the ITO electrode would not, by itself, eliminate gain narrowing.

6. Conclusions and prospects for polymer laser diodes

In order to achieve an electrically pumped polymer laser diode, carrier concentrations sufficient to produce lasing must be demonstrated by electrical pumping. Based on the photon densities at threshold with optical pumping and assuming an electroluminescence (EL) quantum efficiency of a few per-

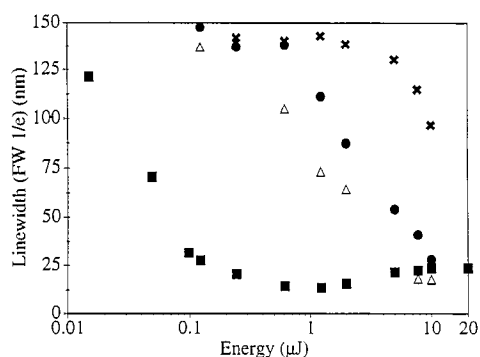


Fig. 5. Linewidth as a function of pump energy per pulse for BuEH-PPV-based waveguides: BuEH-PPV on glass (squares), BuEH-PPV on ITO (crosses), ~ 90 nm PVK and BuEH-PPV on ITO (circles), and ~ 340 nm PVK and BuEH-PPV on ITO (triangles).

cent, the transient current densities necessary to reach the threshold for lasing are estimated to be a few thousand A cm^{-2} . Current densities of 100 A cm^{-2} have been reported in electrically pulsed MEH-PPV polymer LEDs when operated in pulsed mode with low duty cycle [20]; the corresponding peak brightness was 10^6 cd m^{-2} [21]. Moreover, a recent report of current densities of 10^4 A cm^{-2} using STM-induced polymer EL [22] provides further confidence that, with small active areas, low duty cycles, good thermal management, and reductions in lasing threshold with further improvements in high- Q resonant structures, sufficiently high current densities should be accessible.

Recent progress in GaN technology has enabled the development of compact, bright, and highly efficient blue LEDs [23] and blue laser diodes [24] using InGaN quantum-well structures. By combining the high-efficiency PL from semiconducting polymers with the emission from InGaN LEDs, hybrid LEDs can be fabricated which emit white light or light of any color; the InGaN LED provides the blue component and, simultaneously, serves as the short-wavelength pump source for exciting the PL of the polymer film(s) [25].

The achievement of compact photopumped hybrid InGaN/polymer electrically pumped laser diodes with colors spanning the visible spectrum is an attractive possibility. The typical c.w. power output of a 450 nm emitting LED is 5 mW over a device area of $350 \mu\text{m}^2$, which corresponds to an energy density of $0.04 \mu\text{J cm}^{-2}$ for a duration of 10 ns. The peak power has been further increased by one order of magnitude under pulsed operation, approaching the thresholds in the optically pumped lasing experiments. By improving materials and resonant structures, and or by using InGaN laser diodes which are expected to be commercially available in the near future, laser action of the polymer under blue or ultraviolet pumping by InGaN can be anticipated. A novel extension of this concept is to combine the EL of InGaN LEDs or laser diodes with single-color or multi-color arrays of polymer microresonators, with the latter offering the possibility of giving coherent white laser light.

Semiconducting polymers comprise a unique class of solid-state laser materials with emission that spans the entire visible spectrum. Because of their strong absorption, high density of chromophores, and Stokes-shifted luminescence, luminescent semiconducting polymers have potential as laser media with extremely low thresholds, even in submicron-thick films. A new generation of semiconducting polymer laser diodes, obtained either by electrically pumping the semiconducting polymer or the InGaN component in a hybrid InGaN/polymer device, offers promise for novel, full-color narrowband sources for the future.

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References

- [1] A.J. Heeger, S. Kivelson, J.R. Schrieffer and W.-P. Su, *Rev. Mod. Phys.*, **60** (1988) 781.
- [2] F. Hide, B.J. Schwartz, M.A. Díaz-García and A.J. Heeger, *Chem. Phys. Lett.*, **256** (1986) 424.
- [3] F. Hide, M.A. Díaz-García, B.J. Schwartz, M.R. Andersson, Q. Pei and A.J. Heeger, *Science*, **273** (1996) 1833.
- [4] M.A. Díaz-García, F. Hide, B.J. Schwartz, M.R. Andersson, Q. Pei and A.J. Heeger, *Synth. Met.*, **84** (1997) 455.
- [5] N. Tessler, G.J. Denton and R.H. Friend, *Nature*, **382** (1996) 695.
- [6] M.A. Díaz-García, F. Hide, B.J. Schwartz, M.D. McGehee, M.R. Andersson and A.J. Heeger, *Appl. Phys. Lett.*, **70** (1997) 3191.
- [7] H.-J. Brouwer, V.V. Krasnikov, A. Hilberer, J. Wildeman and G. Hadziioannou, *Appl. Phys. Lett.*, **66** (1995) 3404.
- [8] W. Holzer, A. Penzkofer, S.-H. Gong, A. Bleyer and D.D.C. Bradley, *Adv. Mater.*, **8** (1996) 974.
- [9] H.J. Brouwer, V.V. Krasnikov, A. Hilberer and G. Hadziioannou, *Adv. Mater.*, **8** (1996) 935.
- [10] S.V. Frolov, M. Ozaki, W. Gellerman, Z.V. Vardeny and K. Yoshino, *Jpn. J. Appl. Phys.*, **35** (1996) L1371.
- [11] (a) M. McGehee, F. Hide, M.A. Díaz-García, B.J. Schwartz, D. Moses and A.J. Heeger, *Bull. Amer. Phys. Soc.*, **42** (1997) 645. (b) M. McGehee et al., submitted for publication.
- [12] A.E. Siegman, *Lasers*, University Science Books, Mill Valley, CA, 1986.
- [13] S.V. Frolov, W. Gellerman, M. Ozaki, K. Yoshino and Z.V. Vardeny, *Phys. Rev. Lett.*, **78** (1997) 729.
- [14] G.H. Gelinck, J.M. Warman, M. Remmers and D. Neher, *Chem. Phys. Lett.*, **265** (1997) 320.
- [15] H. Kogelnik, in T. Tamir (ed.), *Topics in Applied Optics: Integrated Optics*, Springer, Berlin, 1979.
- [16] B.J. Schwartz, F. Hide, M.R. Andersson and A.J. Heeger, *Chem. Phys. Lett.*, **265** (1997) 327.
- [17] U. Brackmann, *Lambdachrome Laser Dyes*, Lambda Physik, Göttingen, 1994.
- [18] N.C. Greenham et al., *Chem. Phys. Lett.*, **241** (1995) 89.
- [19] K.L. Chopra, S. Major and D.K. Pandya, *Thin Solid Films*, **102** (1983) 1.
- [20] D. Braun, D. Moses, C. Zhang and A.J. Heeger, *Appl. Phys. Lett.*, **61** (1992) 3902.
- [21] (a) A.J. Heeger and G. Yu, *Mater. Res. Soc. Meet.*, Boston, MA, USA, 2 Dec., 1996. (b) R.H. Friend, *Mater. Res. Soc. Meet.*, Boston, MA, USA, 2 Dec., 1996.
- [22] D.G. Lidzey, D.D.C. Bradley, S.F. Alvarado and P.F. Seidler, *Nature*, **386** (1997) 135.
- [23] S. Nakamura, M. Senoh, N. Iwasa, S. Nagahama, T. Yamada and T. Mukai, *Jpn. J. Appl. Phys.*, **34** (1995) L1332.
- [24] S. Nakamura et al., *Appl. Phys. Lett.*, **70** (1997) 868.
- [25] F. Hide, P. Kozodoy, S.P. DenBaars and A.J. Heeger, *Appl. Phys. Lett.*, **70** (1997) 2664.