

New Developments in the Photonic Applications of Conjugated Polymers

FUMITOMO HIDE, MARÍA A. DÍAZ-GARCÍA,
BENJAMIN J. SCHWARTZ,[†] AND
ALAN J. HEEGER*

*Institute for Polymers and Organic Solids,
University of California, Santa Barbara,
Santa Barbara, California 93106-5090*

Received January 28, 1997

I. Semiconducting Polymers as Materials for "Plastic" Photonics Devices

Solid-state photonic devices are a class of devices in which the quantum of light, the photon, plays a role. Because the interband optical transition (absorption and/or emission) is involved in photonic phenomena and because photon energies from near-infrared to near-ultraviolet are of interest, the relevant materials are semiconductors with band gaps in the range from 1 to 3 eV. Typical *inorganic* semiconductors used for photonic devices are Si, Ge, and Group III–V and Group II–VI alloys.¹

Conjugated polymers are a novel class of semiconductors that combine the optical and electronic properties of semiconductors with the processing advantages and mechanical properties of polymers. Important examples of polymers within this class include poly(*p*-phenylenevinylene) (PPV), poly(*p*-phenylene) (PPP), and polyfluorene (PF) derivatives whose molecular structures are shown in

Fumitomo Hide received his B.S. degree in physics from MIT (1991) and his Ph.D. in physics from UC Santa Barbara (1997). From 1991 to 1993, he was with the Sony Research Center (Japan). He is currently a visiting postdoctoral researcher at the Materials Research Laboratory and the Institute for Polymers and Organic Solids, UC Santa Barbara. He has concentrated on semiconducting polymer-based devices and most recently on light amplification and lasing from luminescent semiconducting polymers.

María A. Díaz-García was graduated in physics in 1991 and received her Ph.D. in 1995, both at the Autonomous University of Madrid (Spain). Presently she is a postdoctoral researcher at the Institute for Polymers and Organic Solids, UC Santa Barbara. Her current research interests are in the nonlinear optical properties of conjugated polymers (and oligomers) and on stimulated emission, light amplification, and lasing from luminescent semiconducting polymers.

Benjamin J. Schwartz received his B.S. degree in physics and chemistry at the University of Michigan in 1986 and his Ph.D. in chemistry at UC Berkeley, in 1992. He subsequently held postdoctoral positions at the University of Texas at Austin and at UC Santa Barbara, before accepting a faculty position in Chemistry at UCLA. His research interests lie in experimental and theoretical studies of solution-phase chemical reaction dynamics as well as in the photophysics of conjugated polymers.

Alan J. Heeger is Professor of Physics, Professor of Materials, and Director of the Institute for Polymers and Organic Solids at UC Santa Barbara. He has been at UC Santa Barbara since 1982, following a long career at the University of Pennsylvania (1962–1982). His current research interests are in the electronic, optical, and nonlinear optical properties of semiconducting and metallic polymers with the goal of developing these novel materials for use in commercial applications. UNIAx Corp., which he co-founded in 1990, is currently focusing on bringing "plastic electronics" devices to market. He is the recipient of numerous awards and prizes including the Balzan Prize in 1995.

Figure 1. The relative simplicity with which high photoluminescence (PL) efficiency polymers of different colors can be achieved is in stark contrast to inorganic semiconductors, where, for example, bright blue light emitting diodes (LEDs) were not available until recently because of the difficulties in growing InGaN films.²

Most of the photonic phenomena known in conventional inorganic semiconductors have been observed in these semiconducting polymers. The dream of using such materials in high-performance "plastic" photonic devices is rapidly becoming reality: high-performance photonic devices fabricated from conjugated polymers have been demonstrated, including diodes,³ light-emitting diodes,⁴ photodiodes,⁵ field-effect transistors,⁶ polymer grid triodes,⁷ light-emitting electrochemical cells,⁸ and optocouplers,⁹ i.e., all the categories that characterize the field of photonic devices. These polymer-based devices have reached performance levels comparable to or even better than those of their inorganic counterparts. For a recent review of progress in plastic photonic devices fabricated with semiconducting polymers, see ref 10.

II. Conjugated Polymers as Laser Materials

Notably absent from the list of conjugated polymer based devices given above, however, is the semiconducting polymer laser. In this Account, we focus on recent progress in the rapidly emerging area of conjugated polymers as materials for thin-film solid-state lasers.

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^* (interband) transition of these quasi-one-dimensional semiconducting polymers, the absorption coefficient (α) is large, typically $\alpha \approx 10^5$ cm⁻¹ or greater.¹¹ To first order, the cross-section for stimulated emission (SE) is the same as that for absorption, so the gain length (defined as $l_g = 1/g$, where g is

[†] Permanent address: Department of Chemistry and Biochemistry, UCLA, Los Angeles, CA 90095-1569.

- (1) Sze, S. M. *Physics of Semiconductor Devices*; Wiley: New York, 1981; Part 5.
- (2) Morkoç, H.; Mohammad, S. N. *Science* **1995**, *267*, 51.
- (3) Tomozawa, H.; Braun, D.; Phillips, S.; Heeger, A. J.; Kroemer, H. *Synth. Met.* **1987**, *22*, 63.
- (4) (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539. (b) Braun, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1982. (c) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477.
- (5) (a) Yu, G.; Heeger, A. J. *J. Appl. Phys.* **1995**, *78*, 4510. (b) Halls, J. J. M.; Walsh, C. A.; Marseglia, E. A.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Nature* **1995**, *376*, 498. (c) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789.
- (6) (a) Burroughes, J. H.; Jones, C. A.; Friend, R. H. *Nature* **1988**, *335*, 137. (b) Garnier, F.; Hajlaoui, R.; Yasser, A.; Srivastava, P. *Science* **1994**, *265*, 1684. (c) Brown, A. R.; Pomp, A.; Hart, C. M.; de Leeuw, D. M. *Science* **1995**, *270*, 972. (d) Torsi, L.; Dodabalapur, A.; Rothberg, L. J.; Fung, A. W. P.; Katz, H. E. *Science* **1996**, *272*, 1462.
- (7) Yang, Y.; Heeger, A. J. *Nature* **1994**, *372*, 344.
- (8) (a) Pei, Q.; Yu, G.; Zhang, C.; Yang, Y.; Heeger, A. J. *Science* **1995**, *269*, 1086. (b) Pei, Q.; Yang, Y.; Yu, G.; Zhang, C.; Heeger, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 3922.
- (9) Yu, G.; Pakbaz, K.; Heeger, A. J. *J. Electron. Mater.* **1994**, *23*, 925.
- (10) Yu, G.; Heeger, A. J. In *The Physics of Semiconductors*; Schlegler, M., Zimmerman, R., Eds.; World Scientific: Singapore, 1996; Vol. 1, p 35.
- (11) Heeger, A. J.; Kivelson, S.; Schrieffer, J. R.; Su, W.-P. *Rev. Mod. Phys.* **1988**, *60*, 781.

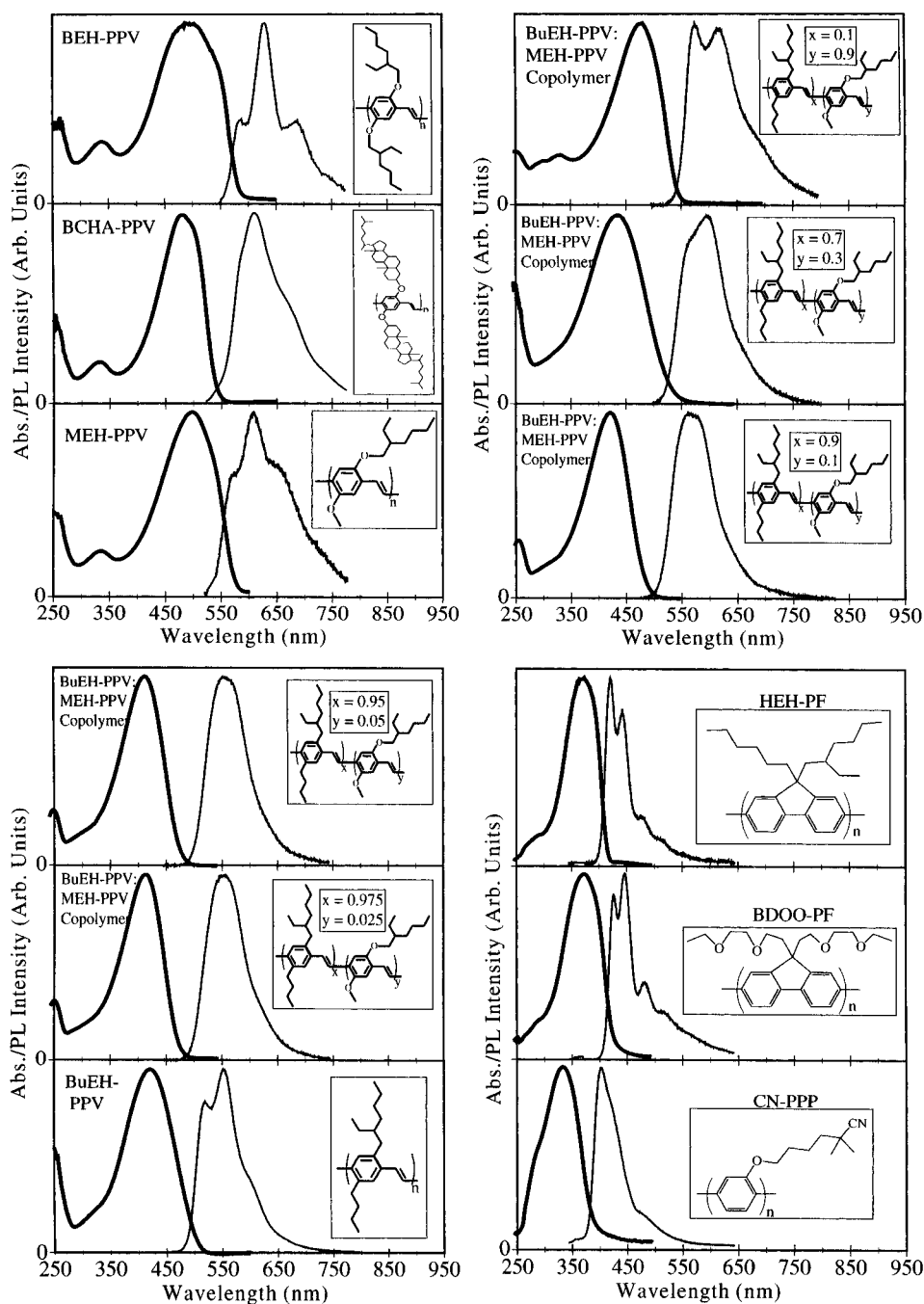


FIGURE 1. Absorption (heavy smooth curves) and photoluminescence (thin, slightly noisy curves) spectra of neat thin films of BuEH-PPV, BCHA-PPV, MEH-PPV, BEH-PPV, BuEH-PPV/MEH-PPV copolymers at different monomer ratios, HEH-PF, BDOO-PF, and CN-PPP. Insets: molecular structures. See Table 1 for full chemical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

the gain) should be essentially equal to the absorption length scaled by the fraction of chromophores in the excited state.¹² 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.

The observation of laser emission from MEH-PPV (see Figure 1 and Table 1 for full chemical name) in dilute solution in an appropriate solvent¹³ established a direct analogy between solutions of polymers and laser dyes for

the first time. Although laser dye molecules also have a Stokes shift which facilitates the achievement of 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 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 (less than

(12) Yariv, A. *Quantum Electronics*, 3rd. ed.; Wiley: New York, 1989.

(13) Moses, D. *Appl. Phys. Lett.* **1992**, *60*, 3215.

Table 1

material	peak PL emission (nm)	λ_{pump} (nm)	energy threshold ($\mu\text{J}/\text{pulse}$)	final line width (nm)	film thickness (nm)	cutoff thickness (nm)	solvent
BuEH-PPV ^a	520, 560	435	0.4 ± 0.2 0.2 ± 0.1	12 9	126–252 87–208	106 ≤ th ≤ 126 65 ≤ th ≤ 87	THF <i>p</i> -xylene
BCHA-PPV ^b	540, 630 (sh)	532	1.0 ± 0.4	11	277–650	160 ≤ th ≤ 277	THF
MEH-PPV ^c	585, 625	532	1.1 ± 0.4	17	87–405	53 ≤ th ≤ 87	THF
			3	50	355	<355	CB
			4	55	325	<325	<i>p</i> -xylene
BEH-PPV ^d	580, 650	532	0.5	13	300	<300	THF
M3O-PPV ^e	530, 620	532	4	16	310	<310	THF
BuEH-MEH copolymers ^f							
10:90	580, 625	532	3.2	23	330	<330	THF
70:30	565, 600	532	1.0	15	420	<420	THF
90:10	550, 580 (sh)	435	1.0	20	370	<370	THF
95:5	545, 580 (sh)	435	1.6	20	450	<450	THF
97.5:2.5	540, 570 (sh)	435	1.0	18	500	<500	THF
HEH-PF ^g	425, 445	355	4.2	12	120	<120	THF
BDOO-PF ^h	430, 450, 540	355	2.3	7			THF
CN-PPP ⁱ	420	355	4	12	100	<100	THF
DCM/PS ^j (2.6% w/v)	640	532	400 ± 150	23	390–4800	260 ≤ th ≤ 390	THF

^a Poly(2-butyl-5-(2'-ethylhexyl)-1,4-phenylenevinylene), see Figure 1a (inset). ^b Poly(2,5-bis(cholestanoxyl)-1,4-phenylenevinylene), see Figure 2b (inset). ^c Poly(2-methoxy-5-((2'-ethylhexyl)oxy)-1,4-phenylenevinylene), see Figure 3 (inset). ^d Poly(2,5-bis((2'-ethylhexyl)oxy)-1,4-phenylenevinylene). ^e Poly(2-methoxy-5-(3'-octyloxy)-1,4-phenylenevinylene). ^f Copolymers synthesized from varying ratios of BuEH-PPV and MEH-PPV monomers. ^g Poly(9-hexyl-9-(2'-ethylhexyl)fluorene-2,7-diyl). ^h Poly(9,9-bis(3,6-dioxaocetyl)fluorene-2,7-diyl). ⁱ Poly(2-((6'-cyano-6'-methylheptyl)oxy)-1,4-phenylene). ^j 4-(Dicyanomethylene)-2-methylene-2-methyl-6-(4-(dimethylamino)styryl)-4*H*-pyran.

1%) in polystyrene;¹⁴ these thick (~100 μm) films contain a dispersion of TiO₂ nanoparticles which confine the emitted photons by multiple scattering so that the distance traveled in the medium exceeds the gain length. Photopumped gain narrowing was subsequently reported for submicron thick films, neat and undiluted, of over a dozen soluble conjugated polymers, including PPV, PPP, and PF derivatives, in planar waveguide structures.^{15,16} Moreover, lasing has been observed in microcavities from PPV¹⁷ and a soluble PPV derivative, BuEH-PPV (see Figure 1 and Table 1).¹⁸ New polymers have been developed that also show spectral narrowing above threshold in solutions^{19,20} and in the solid state.^{21,22}

Gain narrowing refers to the line width narrowing of the emission (PL) spectrum above a threshold optical pump excitation energy. The narrowing is an indication of light amplification by stimulated emission; when light propagates in a medium with gain, the intensity will grow as $\exp(gl)$, where $g(\lambda)$ is the gain at wavelength λ and l is the path length traveled in the gain medium. If $g(\lambda)$ is maximum at $\lambda = \lambda_0$, the exponentially amplified spectrum will be gain narrowed and centered at λ_0 . Achievement of gain narrowing requires that two criteria be fulfilled:

(1) The active polymer medium must exhibit SE under optical or electrical excitation. Many semiconducting polymers fall into this class and are suitable as the active

medium for plastic lasers. The chemical structures, absorption spectra, and PL spectra for several of these luminescent conjugated polymers (and copolymers) are presented in Figure 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. Structures appropriate for amplified spontaneous emission (ASE) include planar waveguides. For polymer lasers, optical feedback has been provided by microcavities^{17,18} and planar waveguides with distributed feedback.²³

The instrumentation for gain-narrowing experiments using thin solid film waveguides has been described in detail elsewhere.¹⁴ Some details are important for calibrating the meaning of the observed thresholds. 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. For the experiments at UC Santa Barbara, the excitation source (the pump) 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 H₂ cell pumped at 532 nm was also used. The energy per pulse was controlled with calibrated neutral density filters.

Initial experiments^{15,16} focused on BuEH-PPV, which has a high PL efficiency (η_{PL}) of 62%²⁴ and a relatively long SE decay time (~60 ps) in neat films.²⁵ The PL spectrum evolution for a neat film of BuEH-PPV, 210 nm thick, is shown as a function of the pump energy per pulse in Figure 2a. As the pump energy is increased, a gain-narrowed peak rises out of the broad emission spectrum until, at sufficiently high energies, only the gain-narrowed

(14) Hide, F.; Schwartz, B. J.; Diaz-García, M. A.; Heeger, A. J. *Chem. Phys. Lett.* **1996**, *256*, 424.

(15) Hide, F.; Diaz-García, M. A.; Schwartz, B. J.; Andersson, M. R.; Pei, Q.; Heeger, A. J. *Science* **1996**, *273*, 1833.

(16) Diaz-García, M. A.; Hide, F.; Schwartz, B. J.; Andersson, M. R.; Pei, Q.; Heeger, A. J. *Synth. Met.* **1997**, *84*, 455.

(17) Tessler, N.; Denton, G. J.; Friend, R. H. *Nature* **1996**, *382*, 695.

(18) Diaz-García, M. A.; Hide, F.; Schwartz, B. J.; McGehee, M. D.; Andersson, M. R.; Heeger, A. J. *Appl. Phys. Lett.* **1997**, *70*, 3191.

(19) Brouwer, H.-J.; Krasnikov, V. V.; Hilberer, A.; Wildeman, J.; Hadziioannou, G. *Appl. Phys. Lett.* **1995**, *66*, 3404.

(20) Holzer, W.; Penzkofer, A.; Gong, S.-H.; Bleyer, A.; Bradley, D. D. C. *Adv. Mater.* **1996**, *8*, 974.

(21) Brouwer, H. J.; Krasnikov, V. V.; Hilberer, A.; Hadziioannou, G. *Adv. Mater.* **1996**, *8*, 935.

(22) Frolov, S. V.; Ozaki, M.; Gellerman, W.; Vardeny, Z. V.; Yoshino, K. *Jpn. J. Appl. Phys.* **1996**, *35*, L1371.

(23) McGehee, M.; Hide, F.; Diaz-García, M. A.; Schwartz, B. J.; Moses, D.; Heeger, A. J. *Bull. Am. Phys. Soc.* **1997**, *42*, 645.

(24) Andersson, M. R.; Yu, G.; Heeger, A. J. *Synth. Met.* **1997**, *85*, 1275.

(25) Schwartz, B. J.; Hide, F.; Andersson, M. R.; Heeger, A. J. *Chem. Phys. Lett.* **1997**, *265*, 327.

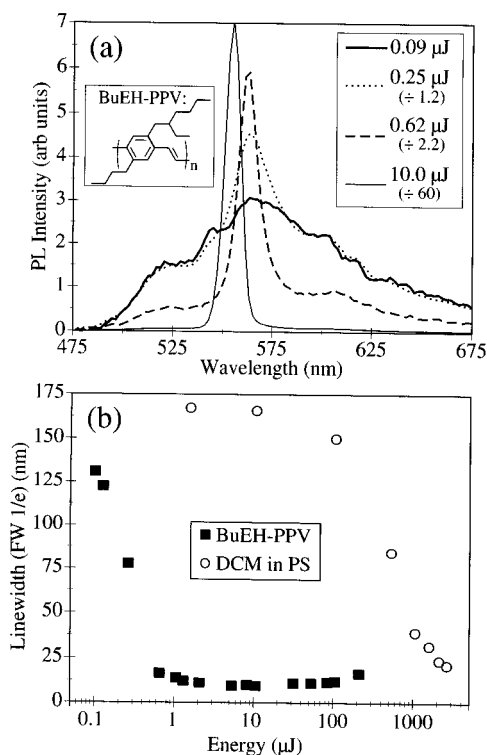


FIGURE 2. (a) Photoluminescence spectrum of 210 nm BuEH-PPV neat film on glass (spin-cast from *p*-xylene solution) at various pump pulse energies both above (10.0 μJ , thin solid curve; 0.62 μJ , dashed curve) and below (0.25 μJ , dotted curve; 0.09 μJ , thick solid curve) the gain-narrowing threshold. Inset: molecular structure of BuEH-PPV. (b) Evolution of the line width (full width at 1/e height) as a function of pump pulse energy (on a log scale) for the BuEH-PPV sample of part a (squares), and for comparison, a 2.6 wt % film of DCM laser dye in polystyrene (open circles) of 3600 nm thickness with comparable optical density to the BuEH-PPV film.

peak survives while the broad tails of the PL are completely suppressed. This dramatic collapse of the line width (from 130 to 9 nm) at remarkably low pump energies ($\leq 1 \mu\text{J}/\text{pulse}$) indicates that these undiluted thin films have short gain lengths. A blue shift of the emission peak at higher energies is also evident in Figure 2a; the blue shift of the emitted radiation suggests that SE occurs on a time scale faster than the spectral diffusion which occurs during the first few tens of picoseconds following photoexcitation.¹⁴ Figure 2b displays the line width of the PL as a function of pump pulse energy, demonstrating a well-defined threshold for spectral narrowing.

If the gain lengths are indeed in the micron or submicron regime, the energy threshold for gain narrowing should be much lower than for conventional laser materials. For reference, therefore, we tested the laser dye DCM (see Table 1) suspended in films of polystyrene (PS) with optical densities comparable to that of the 210 nm BuEH-PPV film of Figure 2. Since dye molecules are known to undergo concentration quenching, the DCM concentration (2.6%) in PS was optimized for maximum luminescence. Although the DCM concentration is more than 2 orders of magnitude higher than that used in typical dye lasers, the threshold for gain narrowing is over 1000 times higher than that of BuEH-PPV, as shown in Figure 2b. Thus, conjugated polymers provide the intense absorption and emission characteristics of organic dyes, but with the

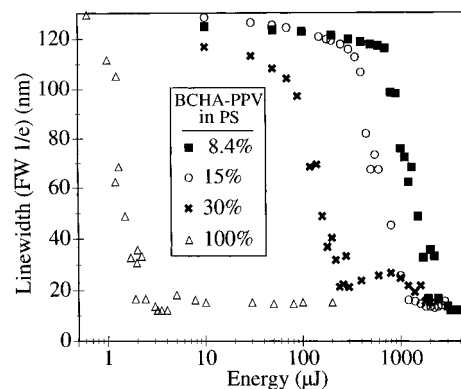


FIGURE 3. Emission line width as a function of pump pulse energy (on a log scale) for various BCHA-PPV/polystyrene blend films at different BCHA-PPV concentrations: 8.4% (squares), 15% (open circles), 30% (crosses), and neat (100%) (open triangles).

substantial advantage of having a much higher density of chromophores in the solid state.

We have explored gain narrowing from a number of PPV, PPP, and PF derivatives;^{15,26} the corresponding $\pi-\pi^*$ energy gaps span the visible spectrum. The full chemical names and gain-narrowing performance parameters are given in Table 1. The very low energy thresholds for gain narrowing indicate that semiconducting polymers comprise a class of promising laser materials with emission spectra that span the full range of the visible portion of the spectrum.

The data in Figure 3 demonstrate the advantages of the high density of chromophores characteristic of semiconducting polymers. The line width vs pump energy of films of varying BCHA-PPV concentration diluted in PS are shown in Figure 3. Upon increasing the concentration of BCHA-PPV in the film from 8.4% to 100% (a factor of 12), the threshold energy decreased by 3 orders of magnitude, to a minimum of 1.3 $\mu\text{J}/\text{pulse}$ for the neat film.

III. Amplified Spontaneous Emission and Gain Narrowing in Planar Waveguides

Asymmetric planar waveguides formed from the refractive index mismatch at the polymer/air and polymer/substrate interfaces of a thin film provide a straightforward and relatively simple method for extending the path length of the emitted photons in the gain medium. The role of waveguiding in optically pumped polymer films has been carefully documented. The results prove that extension of the optical path by waveguiding plays an important role in the observed gain-narrowing behavior in thin-film samples of this class of plastic laser materials.

In general, 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: air/neat polymer film/glass. For this type of asymmetric thin-film structure, a cutoff film thickness (h_{cutoff}) exists, below

(26) Among the PPV derivatives are several copolymers synthesized from varying ratios of BuEH-PPV and MEH-PPV monomers.

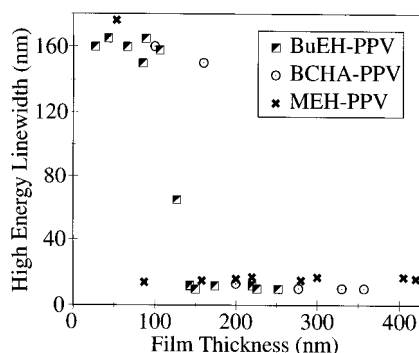


FIGURE 4. Line width of the PL spectrum at a high pump energy ($\geq 10 \mu\text{J}$ per pulse) as a function of the film thickness for BuEH-PPV (half-filled squares; 435 nm excitation), BCHA-PPV (dotted circles; 532 nm excitation), and MEH-PPV (heavy crosses; 532 nm excitation) films spin-cast from THF on glass substrates.

which the fundamental mode cannot propagate:²⁷

$$h_{\text{cutoff}} = \lambda / [2\pi(n_f^2 - n_s^2)^{1/2}] \tan^{-1} [(n_s^2 - n_c^2)/(n_f^2 - n_s^2)]^{1/2} \quad (1)$$

where l is the wavelength of the guided light and the subscripts c, f, and s refer to cladding, film, and substrate, respectively. In the present case c = air, f = neat polymeric film, and s = glass. The refractive indices of BuEH-PPV and BCHA-PPV films were determined from modal waveguide characterization at 633 nm. The refractive indices in the plane of the film were determined to be $n = 1.69$ for BuEH-PPV and $n = 1.60$ for BCHA-PPV. Using the in-plane values of n in eq 1, the calculated h_{cutoff} values are 120 and 200 nm for BuEH-PPV and BCHA-PPV films on glass, respectively.

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 plotted the high-energy ($\geq 10 \mu\text{J}$) PL line width as a function of the film thickness for each of these three polymers in Figure 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 values calculated from the asymmetric waveguide cutoff formula, eq 1. 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.

Additional experiments were performed to verify the role of waveguiding in optically pumped thin polymer films. A BuEH-PPV/glass sample which was too thin (43 nm) to show gain narrowing as an asymmetric waveguide in air was immersed in a solvent that did not dissolve the polymer and which was approximately index matched to the glass substrate (cyclohexanone, $n = 1.49$). This produced a symmetric waveguide configuration, where no minimum film thickness for waveguiding is expected. Once in the solvent, the film showed dramatic gain

narrowing. This process is reversible: removing the film from the index matching solvent and drying caused the laser-like behavior to disappear. This observation eliminates other possible explanations for the thickness dependence of the gain narrowing, such as loss of optical density as the film thickness decreases. The thin-film waveguide structure is critical to the production of gain narrowing: Even with the presence of SE and a sufficient density of chromophores, the optical path of the emitted light does not exceed the gain length at low pump energies without waveguiding. Since the coupling between the emissive dipoles in the polymer film could not be altered by merely changing the index of refraction of the external medium, the possibility of superfluorescent emission²⁸ as the mechanism of gain narrowing is eliminated.

IV. Comparison of Gain Narrowing in Waveguides and Microcavities

A detailed comparison of the emission from conjugated polymer lasers constructed from microcavities (~ 470 nm thick polymer layer between a highly reflective distributed Bragg reflector, DBR, and a 60 nm silver mirror) to the gain-narrowed PL produced in thin-film planar waveguides was recently completed.¹⁸ The quality of the microcavity polymer laser is strongly dependent on matching the microcavity mode to the gain maximum of the PL polymer. For BuEH-PPV, the threshold for gain-narrowed emission in waveguides and microcavities was found to be approximately the same. Moreover, there are advantages for each approach.

The DBR mirrors have reflectivities nominally greater than 99% at normal incidence from 488 to 694 nm. The high reflectivity over such a broad wavelength range results from the many layers with different thicknesses (chirped DBR). As a result, the microcavity supports several modes.^{17,18} Waveguides and microcavities consisted of simple layered structures: glass/BuEH-PPV/air for the waveguides and DBR/PVK/BuEH-PPV/Ag or DBR/BuEH-PPV/PVK/Ag for the microcavities, with poly(*N*-vinylcarbazole) (PVK) as a nonluminescent and nonabsorptive buffer layer. BuEH-PPV waveguides had gain narrowing thresholds as low as $\approx 0.05 \mu\text{J/pulse}$.

Since microcavities have relatively high Q and efficiently couple emitted photons to only a few cavity modes,²⁹ the emission peaks are quite narrow (≤ 7 nm) even below threshold. Above threshold, the emission peak nearest the gain maximum (550 nm for BuEH-PPV) grows in intensity more rapidly than the other emission peaks as the pump energy increases. Thus, following Tessler et al.,¹⁷ the mode ratio is defined as the ratio of the integrated power of the lasing mode to that of one of the spontaneous emission modes.

The emission modes from a BuEH-PPV microcavity (~ 340 nm of PVK between the BuEH-PPV and Ag mirror), with intensities scaled for clarity, are shown in Figure 5. All pump energies were corrected for the transmission of the silver. There is a strong emission peak around 552 nm, close to the gain maximum of BuEH-PPV, and observ-

(27) Kogelnik, H. In *Topics in Applied Optics: Integrated Optics*; Tamir, T., Ed.; Springer-Verlag: Berlin, 1979; Chapter 2.

(28) Frolov, S. V.; Gellerman, W.; Ozaki, M.; Yoshino, K.; Vardeny, Z. V. *Phys. Rev. Lett.* **1997**, *78*, 729.

(29) Yokoyama, H. *Science* **1992**, *256*, 66.

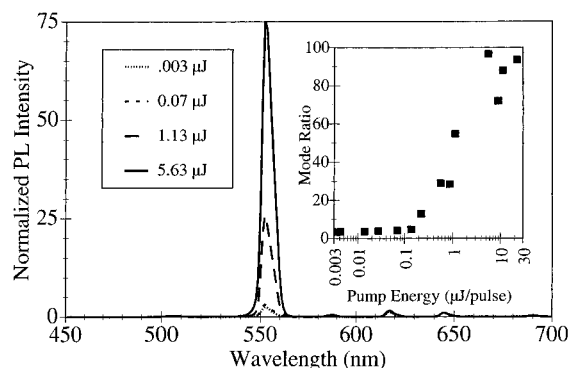


FIGURE 5. Emission spectra from a microcavity: DBR/BuEH-PPV/PVK/Ag at various pump energies. The PVK layer is ~ 340 nm thick. Inset: ratio of integrated intensities (mode ratio) of ~ 552 nm peak to ~ 645 nm peak.

able emission from four other microcavity modes. An abrupt increase in the mode ratio (see inset) is observed near $0.1 \mu\text{J}/\text{pulse}$, the lasing threshold. Note that the mode ratio approaches 100 at pump energies which are above threshold but still fairly low ($\sim 60 \mu\text{J}/\text{pulse}$). Thus, like the waveguides, microcavities can produce single-mode emission with a narrow peak when pumped above threshold.

Varying the thickness of PVK in microcavities provides control over the positions of the allowed modes with respect to the gain maximum of BuEH-PPV. The mode ratio is sensitive to the positions of the cavity modes. If the PVK thickness is adjusted such that a resonance occurs at the maximum gain wavelength of BuEH-PPV, the normalized mode ratio is greatly enhanced, leading to effectively single-mode emission above threshold (cf. Figure 5). Single-mode operation is only realized, however, when the lasing peak is located within ~ 5 nm of the gain maximum. BuEH-PPV microcavities with lasing peaks at wavelengths less than ~ 547 nm or greater than ~ 554 nm showed mode ratios of only about 5, even well above threshold. Hence, to obtain single-mode lasing from microcavities, the cavity design must be optimized to better than about 5 nm.¹⁸ This result is in contrast to the emission from planar waveguides, where single-mode emission is routine.

By interchanging the order of the polymer layers, one can determine whether there is significant quenching when the active polymer is in contact with the Ag mirror. Regardless of the presence of PVK or the proximity of the BuEH-PPV to the Ag mirror, the lasing threshold was around $0.1 \mu\text{J}/\text{pulse}$. There was no indication that thresholds were lower for samples with a PVK buffer layer between the BuEH-PPV and Ag. Thus, although the metal electrode limits the Q of the microcavity, PL quenching by proximity to the metal does not appear to be of major importance.

The angular dependence of the emission from a microcavity with a ~ 900 nm PVK layer between BuEH-PPV and Ag is shown in Figure 6. This structure showed essentially single-mode emission above threshold similar to the data in Figure 5. To measure the angular dependence, the emitted light was collected through a 1 mm pinhole placed ~ 10 cm from the sample, providing angular resolution of $\sim 0.5^\circ$. At pump energies below the

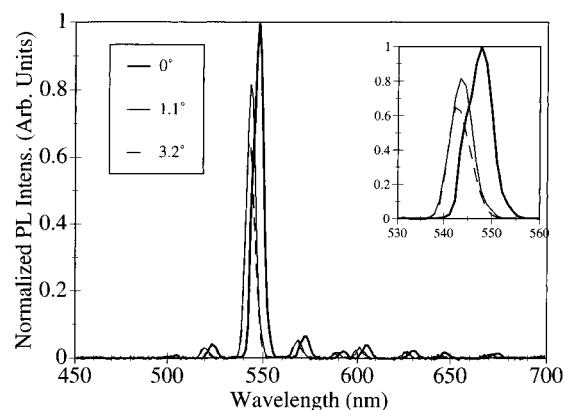


FIGURE 6. External observation angle dependence of emission spectra of a microcavity DBR/BuEH-PPV/PVK/Ag. The PVK layer is ~ 900 nm thick. Inset: expanded view of the lasing peak near 550 nm.

lasing threshold ($0.1 \mu\text{J}/\text{pulse}$), the integrated emission intensity decreased by nearly 1 order of magnitude as the collection angle deviated from 0° to 5° from the normal, a result which indicates fairly high Q . The emission spectra shown in Figure 6 were collected at three different angles at a pump energy ($\sim 10 \mu\text{J}/\text{pulse}$) well above the lasing threshold (see Figure 6 inset). The spectra are scaled such that the intensities of the main peak at below-threshold pumping levels are normalized to the same value (the directionality that is inherent in microcavity structure has been divided out). Figure 6 shows that, above threshold, the normalized intensity of the main peak is reduced by $\sim 35\%$ relative to its below-threshold value as the collection angle is increased from 0° to 3.2° . Thus, in addition to achieving the relatively high degree of directionality expected for microcavities, the directionality is enhanced above the lasing threshold. These observations confirm that the light emitted from optically pumped semiconducting polymer microcavities is laser light.^{17,18}

The lasing thresholds of the microcavities ($\sim 0.1 \mu\text{J}/\text{pulse}$) are comparable to the gain-narrowing thresholds for conjugated polymers in planar waveguides ($0.05 \mu\text{J}/\text{pulse}$). Thus, the optical path length within the gain medium is approximately the same in both structures. Microcavities provide the resonant feedback necessary for "true" lasing, where the emitted laser light is directional and spectrally narrow. These advantages come at a significant expense, however, in device fabrication. In waveguides, which are easily prepared simply by spin-casting a polymer film from solution, luminescence from the polymer is amplified when the distance traveled by the guided light exceeds the gain length. This amplified spontaneous emission is lasing in the original sense of the acronym (laser: light amplification by stimulated emission of radiation) but not in the more stringent sense of modern usage which requires feedback on a well-defined optical mode. Waveguides offer clear advantages for applications that require bright, isotropic, spectrally narrow emission, and microcavities work best for applications where a well-defined beam of emitted light is desired. In both structures, the excited semiconducting polymer leads to amplification with a very short gain length.

V. Conclusions and Future Directions

The observation of optically pumped lasing in undiluted submicron thick films of conjugated polymers offers the promise of constructing laser diodes with such polymers as gain media. To realize this promise, however, carrier concentrations sufficient to produce lasing must be demonstrated by electrical pumping. On the basis of the photon densities at threshold with optical pumping and assuming an electroluminescence (EL) quantum efficiency of a few percent, the transient current densities necessary to reach the threshold for gain narrowing are estimated to be a few thousand amperes per centimeter squared. Current densities of 100 A/cm² have been reported³¹ in electrically pulsed MEH-PPV polymer LEDs when operated in pulsed mode with a low duty cycle;³⁰ the corresponding peak brightness was 10⁶ cd/m². Moreover, a recent report of current densities of 10⁴ A/cm² using STM-induced polymer EL³² provides further confidence that, with small active areas, low duty cycles, and good thermal management, sufficiently high current densities should be accessible.

Construction of a laser diode with a high-*Q* resonant cavity or improved waveguiding structures should provide the required reduction in the lasing threshold. We are presently studying an improved waveguide structure with distributed feedback (DFB) gratings. Initial results indicate that lasing thresholds can perhaps be lowered by 1 order of magnitude compared to those of microcavities.²³ By improving the quality of the waveguide, we expect to lower the DFB lasing threshold even further. High-*Q* "whispering gallery" mode microresonators comprise another class of resonant structures that may be compatible with the inherently short gain lengths in thin undiluted films of conjugated polymers. Photolithographic and self-assembly techniques have been employed to pattern microresonators in dye-doped inert polymer material.³³ The lasing thresholds, however, were not as low as expected because of concentration quenching at the large dye concentrations that were used.³³ Undiluted conjugated polymer microresonators would overcome this difficulty. Examples of possible microresonators include the following: microcylinders formed by polymer coated glass capillaries, optical fibers, and glass wool; microdisks formed by polymer films in PTFE membrane filters or photolithographic patterning of polymer films; and polymer or polymer-coated microspheres.

Microresonator self-assembly mediated by the entropically driven phase segregation of polymer blends is another possibility.³⁴ We are currently addressing all of these avenues.

Recent progress in GaN technology has enabled the development of compact, bright, and highly efficient blue LEDs³⁵ and blue laser diodes³⁶ 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).³⁷ White, green, green-yellow, and yellow emitting InGaN/polymer hybrid LED prototypes have been demonstrated simply by dip-coating prepackaged blue LEDs in the appropriate polymer solutions.

The achievement of compact photopumped hybrid InGaN/polymer electrically pumped laser diodes with colors spanning the visible spectrum is an attractive possibility. The typical CW power output of a 450 nm emitting LED is 5 mW over a device area of (350 μm)², which corresponds to an energy density of 0.04 μJ/cm² for a duration of 10 ns. The peak power has been further increased by 1 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 soon, 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 multicolor arrays of polymer microresonators, with the latter offering the possibility of giving coherent white laser light.

To summarize, semiconducting polymers comprise a unique class of *solid-state* laser materials with emission that spans the entire visible spectrum. Photopumped lasing and light amplification by stimulated emission have been demonstrated in microcavities and waveguides, respectively, with similar thresholds. New approaches are being pursued in an effort to decrease the lasing threshold. 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, narrow-band sources for the future.

We extend our sincere thanks to Dr. M. R. Andersson (Chalmers) and Dr. Q. Pei (UNIAX Corp.) for synthesis of the polymers considered in this work and Prof. S. P. DenBaars (UCSB) for collaborative efforts on the InGaN/conjugated polymer hybrid LED technology. This laser work was supported by the Office of Naval Research (N00014-91-J-1235); work on the InGaN/conjugated polymer hybrid LED was supported by the AFOSR (F49620-96-1-0107). M.A.D.-G. is partially supported by the Government of Spain.

AR9501910

- (30) Braun, D.; Moses, D.; Zhang, C.; Heeger, A. J. *Appl. Phys. Lett.* **1992**, *61*, 3902.
- (31) (a) Heeger A. J.; Yu, G. Materials Research Society Meeting, Boston, MA, December 2, 1996. (b) Friend, R. H. Materials Research Society Meeting, Boston, MA, December 2, 1996.
- (32) Lidzey, D. G.; Bradley, D. D. C.; Alvarado, S. F.; Seidler, P. F. *Nature* **1997**, *386*, 135.
- (33) Kuwata-Gonokami, M.; Jordan, R. H.; Dodabalapur, A.; Katz, H. E.; Schilling, M. E.; Slusher, R. E. *Opt. Lett.* **1995**, *20*, 2093.
- (34) Berggren, M.; Inganäs, O.; Gustafsson, G.; Rasmussen, J.; Andersson, M. R.; Hjertberg, T.; Wennerström, O. *Nature* **1994**, *372*, 444.
- (35) Nakamura, S.; Senoh, M.; Iwasa, N.; Nagahama, S.; Yamada, T.; Mukai, T. *Jpn. J. Appl. Phys.* **1995**, *34*, L1332.
- (36) Nakamura, S.; Senoh, M.; Nagahama, S.; Iwasa, N.; Yamada, T.; Matsushita, T.; Sugimoto, Y.; Kiyoku, H. *Appl. Phys. Lett.* **1997**, *70*, 868.
- (37) Hide, F.; Kozodoy, P.; DenBaars, S. P.; Heeger, A. J. *Appl. Phys. Lett.* **1997**, *70*, 2664.