

Plastic lasers: Semiconducting polymers as a new class of solid-state laser materials

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Abstract

We demonstrate optically pumped lasing in submicron thick films, neat and undiluted, of photoluminescent conjugated polymers. Lasing is evidenced by a dramatic collapse of the emission line width (to as little as 7 nm) at very low pump energy thresholds ($\sim 10 \mu\text{J}/\text{cm}^2$). Laser action is found in over a dozen different conjugated polymers representing a variety of molecular structures, including poly(*p*-phenylenevinylene), poly(*p*-phenylene) and polyfluorene derivatives; lasing wavelengths in these materials span the visible spectrum. The short gain lengths in these conjugated polymers are attributed to the high density of chromophores, the large density of states associated with the interband (π - π^*) transition in quasi-one-dimensional systems, and the Stokes shift which minimizes self-absorption and enhances stimulated emission in the absence of excited state absorption. The observation of lasing in this new class of solid-state laser materials is explained in terms of simple planar waveguiding structures which allow the distance traveled by emitted photons to readily exceed the short intrinsic gain lengths. The dependence of the threshold and the gain narrowed line width on the solvent from which the film is spin cast suggests that chain packing can be used to control lasing in some of these materials. The 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 films.

Keywords: stimulated luminescence; photoluminescence; poly(phenylene vinylene) and derivatives; lasers

1. Introduction

Semiconducting conjugated polymers have been the subject of extensive research as the active media in a variety of optoelectronic devices, including diodes,[1] light emitting diodes,[2] photodiodes,[3] polymer grid triodes,[4] and light emitting electrochemical cells (LECs).[5]

Notably absent from this list of conjugated polymer based devices, however, is the semiconducting polymer laser. Construction of such a laser requires that two criteria be fulfilled: First, the active polymer medium must exhibit stimulated emission (SE) when excited optically or electrically; second, some type of resonant structure must enable the emitted photons to travel a distance greater than the gain length in the excited polymer. Most attempts to construct semiconducting polymer lasers based on high-Q resonant cavities have been hindered by the lack of SE in the polymers being studied.[6] In recent months, however, there has been great progress in demonstrating laser action from conjugated polymers.[7,8] Despite this progress in optically pumped polymer lasers, the achievement of spectrally narrow polymer laser diodes remains an important goal for polymer optoelectronic devices.

In this work, we extend the results presented in initial publications [8] and show that an entire class of neat conjugated polymer films with submicron thickness on appropriate substrates satisfy both the above criteria for lasing and exhibit laser action with optical excitation densities on the order of $10 \mu\text{J}/\text{cm}^2$. We show that many semiconducting polymers, including functionalized poly(*p*-phenylenevinylene) (PPV),[9,10] poly(*p*-phenylene) (PPP),[11] and polyfluorene (PF)[12] derivatives, fall into this class and are suitable as active media for plastic lasers.

Laser emission from conjugated polymers has been reported in dilute solutions in direct analogy with conventional laser

dyes.[13] These observations are consistent with findings from ultrafast spectroscopic experiments that in solutions and dilute blend films, where the polymer chains are isolated, poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) exhibits SE.[14] In neat films of MEH-PPV spin cast from chlorobenzene (CB), however, photoinduced absorption in the same spectral region as the polymer luminescence masks the SE; the photoinduced absorption being the result of electronic interactions between the polymer chains.[14] Femtosecond studies on other polymer systems indicated that most conjugated polymers which exhibit SE in neat films have SE decay times of at most a few ps.[15] Recently, however, we discovered that for the newly synthesized polymer, poly(2-butyl-5-(2'-ethyl-hexyl)-1,4-phenylene vinylene) (BuEH-PPV), SE in neat films persists for over 60 ps,[16] considerably longer than in other polymers.[15] The mechanism for SE quenching via a dynamic blue-shift of the interfering photoinduced absorption was also elucidated.[16] Because of experimental limitations, the 60 ps SE lifetime observed for BuEH-PPV was obtained through optical excitation (310 nm) far above the absorption edge (~ 490 nm), a situation in which previous reports suggest that SE is minimized:[15] presumably under more optimal pumping near the band edge, the SE lifetime of BuEH-PPV could be even longer. These results point to the possibility of synthesizing polymers with long SE times by a judicious choice of functionalized side chains on the conjugated polymer backbone, and indicate that conjugated polymers in the solid-state have the potential to satisfy the first requirement for lasing: the presence of strong SE from the excited state.

The second requirement, that the emitted photons must travel distances longer than the gain length in the excited medium, can be achieved by using resonant structures; for

example, cavities or waveguides.[6,17]

Because dilute blend films of conjugated polymers were known to satisfy the first criterion for lasing (as a result of the inhibition of interchain interactions), a novel approach to solving the problem of optical feedback was developed. Solid-state polymer lasers were fabricated in which the gain material was a dilute blend of MEH-PPV ($\leq 1\%$ by weight) in polystyrene (PS); these thick ($\sim 100 \mu\text{m}$) films also contain a dispersion of TiO_2 nanoparticles which confine the emitted photons by multiple scattering so that the distance traveled in the medium exceeds the gain length.[7]

For neat conjugated polymers, as described in detail here, we use thin film waveguides to confine the emitted light. These waveguides provide an alternate method for achieving path lengths for the emitted photons which exceed the gain length.

In this report, we summarize results which demonstrate a new approach to solving the simultaneous problems of stimulated emission and gain extraction using neat films of conjugated polymers. The high density of chromophores and the large joint density of states associated with the interband (π - π^*) transition in films of these quasi-one-dimensional materials results in a particularly strong absorption from the ground state, with typical absorption lengths of only a few hundred nanometers or even less.[18] Many conjugated polymers exhibit relatively high photoluminescence (PL) efficiencies and have emission that is shifted sufficiently far from the absorption edge that self-absorption is minimal. This allows for enhanced SE in the absence of excited state absorption, as demonstrated for BuEH-PPV.[16] To first order, the cross-section for SE is the same as that for absorption, so the gain length in conjugated polymers should be essentially the same as the absorption length scaled by the fraction of chromophores in the excited state.[17] Thus, semiconducting luminescent polymers offer promise as novel laser materials with gain lengths in the micron or submicron regime. Moreover, because of the processability of soluble conjugated polymers, one can take full advantage of these short gain lengths by fabricating thin film waveguide structures.

We describe experiments demonstrating gain narrowing and laser action in submicron films of various conjugated polymers under optical excitation. The next section describes the experimental methods used for the preparation and optical characterization of the polymer samples. Section 3 explores the gain narrowing behavior of over a dozen different conjugated polymers and copolymers. We investigate their properties in the form of both neat and diluted thin films and compare to films containing a dispersion of DCM (4-dicyanomethylene-2-methyl-6-(*p*-dimethylaminostyryl)-4*H*-pyran) laser dye [19] in a host polymer, polystyrene (PS). Unlike the dye, with conjugated polymers gain narrowing can be observed even when the density of chromophores is maximized by using neat polymer films. By comparing the gain narrowing behavior of different materials, we arrive at some initial generalizations concerning the molecular engineering of polymeric materials for use in plastic lasers. Section 4 examines the role of waveguiding in optically pumped polymer films. By investigating the film thickness dependence of the lasing threshold and making use of index-matched solvents, we show that simple planar waveguiding arising from the refractive index mismatch at polymer/substrate and polymer/air interfaces provides optical path lengths that are resonantly enhanced and sufficient to obtain laser action. In Section 5, we consider the observation that both the index of refraction and lasing behavior of conjugated polymer films depend on the solvent from which the film is cast. These results suggest that chain conformation and morphology may affect SE or waveguiding mechanisms or both, allowing partial control over the extent to which lasing occurs. Finally, Section 6 summarizes

the results, and points out future directions and potential problems that remain for the construction of electrically pumped semiconducting polymer diode lasers.

2. Experimental

Syntheses of the polymers studied here were carried out at either UNIAX Corporation or at the Institute for Polymers and Organic Solids (UCSB). Laser grade DCM dye and polystyrene (MW=50,000) were obtained from Exciton Inc. and Polysciences, Inc., respectively.

Polymer films were prepared in a nitrogen atmosphere by spin casting or drop casting polymer solutions onto appropriate substrates. The films were stored in the inert environment until immediately before use in the optical characterization experiments, which were carried out under ambient conditions. Optical absorption measurements used a HP 4852A UV-Vis spectrometer. Film thicknesses of spin cast films (thicknesses between 27 and 4800 nm) were measured on a Dektak surface profilometer; for drop cast films (thicknesses between 10 and 200 nm), a digital micrometer was used. The refractive indices (n) of the films were determined from modal waveguide characterization by the prism coupling technique [20] in a standard Metricon apparatus.

Neat thin films of the various polymers (PPV, PPP, and PF derivatives) studied here were obtained by spin-casting (spin speeds ranging from 750 to 4800 rpm) polymer solutions (0.5 ~ 5% w/v) from anhydrous tetrahydrofuran (THF), *p*-xylene or chlorobenzene (CB). Spin casting was carried out once or twice over the same substrate, depending on the desired film thickness. Film quality was generally good, with no macroscopic inhomogeneities and a surface roughness of $\leq 10\%$. Glass microscope slides were used as substrates for most of the experiments; in some cases sapphire was employed to provide a higher index material (in order to investigate the role of waveguiding mechanisms). Substrates were cleaned by sonication in common organic solvents prior to use. Similar procedures were followed for preparation of DCM/PS spin cast films, with various DCM/PS concentrations and PS/THF concentrations ranging from 10 to 50 %.

The purity of the THF solvent is especially critical to the production of spin cast polymer films which show gain narrowing. Because of the high affinity of THF for water, exposure of the solvent to ambient conditions before the casting process results in poor quality samples which show no signs of lasing. This problem is avoided through the use of freshly distilled THF and by casting films in an inert atmosphere.

Thin films of BCHA-PPV diluted in PS were obtained by drop casting on glass substrates. A BCHA-PPV/THF solution (3% w/v), and additional THF were combined with a PS/THF concentration of 20% w/v and stirred to yield solutions with BCHA-PPV/PS concentrations of 8.4%, 15%, 30%, and 100%. The resulting blend solutions were mixed thoroughly, drop cast onto glass substrates, and allowed to dry in an inert atmosphere.

The instrumentation for testing the lasing behavior of the conjugated polymer films has been described in detail elsewhere.[7] Films at room temperature were optically pumped at a wavelength appropriate to the polymer absorption spectrum. In a typical experiment, the emitted light was collected from the front face of the sample. The line narrowing effects observed in the polymer films, however, could be detected in all directions and for a variety of pumping geometries. The excitation source was a 10 Hz, Q-switched Nd:YAG laser (Spectra Physics Quanta-Ray DCR-3), which provided ~ 10 ns pulses at either 532 or 355 nm. For some polymers, the first anti-Stokes Raman line (435 nm) from a high pressure H_2 cell pumped with 532 nm light was used. The energy per pulse of the pump was controlled with

calibrated neutral density filters. The incident beam was focused on to the sample (spot size of ~ 1.5 mm) at a 30° angle. The emission that passed through a ~ 2 mm aperture placed normal to the front face of the sample was collected, frequency dispersed in a single monochromator (Spex), and detected by a Peltier-cooled CCD array (Photometrics). A typical experimental run recorded changes in the PL spectrum as a function of the excitation energy per pulse.

3. Gain Narrowing and Lasing in Conjugated Polymers

The basic data set which demonstrates lasing in conjugated polymers is presented in Figure 1. In this figure, the PL spectrum evolution is shown as a function of the pump pulse energy for a 210 nm thick neat film of BuEH-PPV, pumped at 435 nm. As the pump energy is increased, a gain-narrowed peak rises out of the broad emission spectrum, until at sufficiently high energies (\geq a few μJ), only the gain-narrowed laser peak survives and the broad wings of the PL are suppressed. This dramatic collapse of the line width (from 130 nm to 8.5 nm) at very low pumping energies (~ 1 μJ) indicates that these undiluted thin films exhibit laser action with a very short gain length. To make this line narrowing more quantitative, we plot the PL line width [21] of BuEH-PPV against the energy of the pump pulse in Figure 2. The figure demonstrates a well-defined pump energy threshold for line narrowing, a clear signature of laser action.

Another feature evident in Fig. 1 is a small 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 faster than interchain energy migration,[7] and providing another direct signature of laser action. Over a dozen other polymers were investigated, including PPV, poly-*p*-phenylene, and polyfluorene derivatives; the lasing behavior, luminescence properties and chemical names of all these materials are summarized in Table 1.

We have also investigated the performance of copolymers containing varying ratios of BuEH-PPV and MEH-PPV monomers as laser materials.[8] BuEH-PPV showed the lowest lasing threshold among all the polymers studied. By varying the fractional composition of MEH-PPV monomer in a copolymer, we can create low threshold lasing polymers whose molecularly tunable emission spans wavelengths intermediate between the green (pure BuEH-PPV) and orange (pure MEH-PPV) (Table 1).

We note that the copolymers show more robust behavior than either of the pristine polymers alone. BuEH-PPV has a relatively low optical damage threshold in air (~ 100 μJ) in

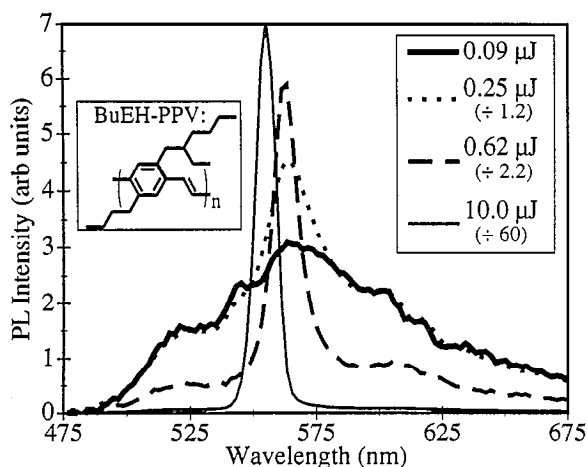


Fig. 1: Photoluminescence spectra of 210 nm thick film of BuEH-PPV spun on glass at various pump energies both above and below the lasing threshold. Inset: Chemical structure of BuEH-PPV.

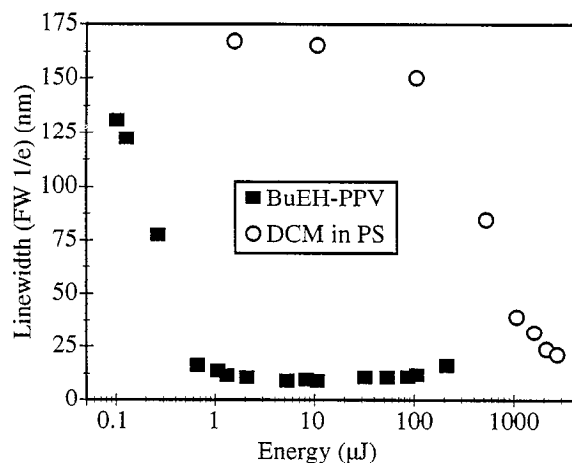


Fig. 2: Evolution of the line width versus pump pulse energy for the BuEH-PPV sample of Fig. 1 (squares) and a 2.6% by weight film of DCM in PS (circles) with a comparable optical density.

optical pumping experiments, and the PL behavior of films of BuEH-PPV appears to degrade somewhat after several days outside the glove box. The addition of even a few percent MEH-PPV into the copolymer with BuEH-PPV leads to both greatly improved air stability and to more than an order of magnitude increase in the optical damage threshold.[8]

For reference, thin films of various concentrations of the laser dye DCM suspended in polystyrene (PS) were also tested (Fig. 2; Table 1). Dye molecules like DCM are known to undergo concentration quenching. Thus, films were prepared with different DCM concentrations; with increasing DCM concentration, the lasing threshold at first decreases and then increases. We chose the highest concentration for which the threshold was still decreasing, 2.6% by weight, for the results presented in Figure 2. The thickness of these films was adjusted to provide optical densities comparable to the BuEH-PPV films discussed in Figs. 1 and 2 above. Although these films have DCM concentrations that are more than 2 orders of magnitude higher than in a typical dye laser, the threshold for gain narrowing is still over 1000 times higher than that of BuEH-PPV. Thus, conjugated polymers 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, resulting in significantly shorter gain lengths.

A high density of chromophores is an important element in the performance of thin film lasers because of the corresponding decrease in the energy threshold for line narrowing. This conclusion is further supported by the experimental results obtained from films of varying BCHA-PPV concentration diluted in PS; Fig. 3 shows the line-narrowing behavior as a function of the BCHA-PPV concentration. Upon increasing the concentration of BCHA-PPV in the film from 8.4% to 100% (a factor of 12) the threshold energy decreased by three orders of magnitude, to a minimum of 1.3 μJ per pulse for the neat film. These results are consistent with the DCM dye results presented in Fig. 2 and illustrate the advantages of using neat and undiluted conjugated polymer films as a laser material. Note that the decrease in lasing threshold with increasing conjugated polymer concentration is highly non-linear. This strongly superlinear behavior is indicative of the exponential sensitivity of laser action on the gain length of the active medium.

4. Waveguiding Mechanisms in Polymer Lasing

In the absence of intentional resonant feedback mechanisms such as those provided by micro-cavities, a method for extending

Material	Peak PL emission (nm)	λ_{pump} (nm)	Energy Threshold ($\mu\text{J}/\text{pulse}$)	Final Linewidth (nm)	Film Thickness Range (nm)	Cutoff Thickness (nm)	Solvent
BuEH-PPV ^a	520, 560	435	0.4 \pm 0.2 0.2 \pm 0.1	12 9	126-252 87-208	106 \leq Th \leq 126 65 \leq Th \leq 87	THF <i>p</i> -xylene
BCHA-PPV ^b	540, 630(sh)	532	1.0 \pm 0.4	11	277-650	160 \leq Th \leq 277	THF
MEH-PPV ^c	585, 625	532	1.1 \pm 0.4 3 4	17 50 55	87-405 355 325	53 \leq Th \leq 87 <355 <325	THF CB <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-PP ^g	425, 445	355	4.2	12	120	<120	THF
BDOO-PP ^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 \pm 150	23	390-4800	260 \leq Th \leq 390	THF

^apoly(2-butyl-5-(2'-ethyl-hexyl)-1,4-phenylene vinylene), see Fig. 1a inset; ^bpoly(2,5-bis(cholestanoxy)-1,4-phenylene vinylene), see Fig. 2b inset; ^cpoly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene), see Fig. 3 inset; ^dpoly(2,5-bis(2-ethyl-hexyloxy)-1,4-phenylene vinylene); ^epoly(2-methoxy-5-(3'-octyloxy)-1,4-phenylene vinylene); ^fcopolymers synthesized from varying ratios of BuEH-PPV and MEH-PPV monomers; ^gpoly(9-hexyl-9-(2'-ethyl-hexyl)-fluorene-2,7-diy); ^hpoly(9,9-bis(3,6-dioxacyl)-fluorene-2,7-diy); ⁱpoly(2-(6'-cyano-6'-methyl-heptyloxy)-1,4-phenylene); ^j4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran

Table 1: Lasing behavior of the different conjugated polymers investigated in this work. Column 1 presents the common name of the polymer; column 2 presents the peaks of each polymer's PL spectrum, including the positions of vibronic shoulders; the pump wavelength used for each polymer is presented in column 3; the threshold for lasing is presented in column 4; the PL line width at energies at least twice that of the threshold energy is given in column 5; column 6 presents the range of film thicknesses investigated in this study; column 7 presents the minimum film thickness necessary to observe gain narrowing for each material; films of each of these materials were spin cast from the solvent presented in column 8.

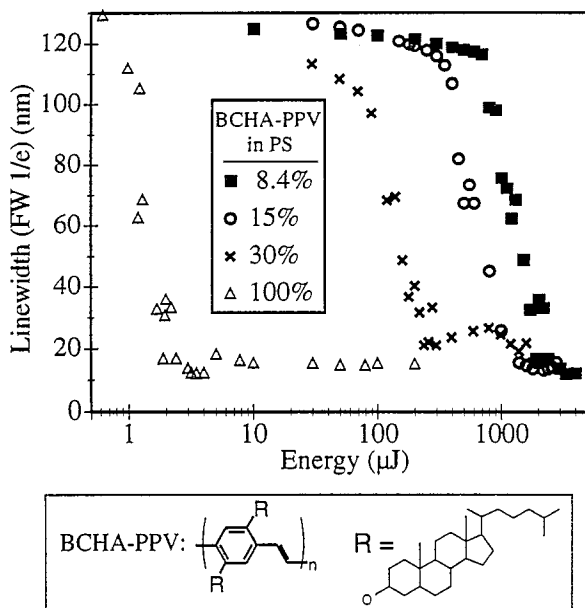


Fig. 3: Emission line width versus pulse energy for BCHA-PPV/PS blend films with different concentrations; structure of BCHA-PPV.

the path length of the emitted photons in the gain medium arises from the natural asymmetric planar waveguide formed from the refractive index mismatch at the polymer/air and/or polymer/substrate interfaces of a thin film. Here, we explore the role of waveguiding in optically pumped polymer film lasers. We examine the dependence of gain narrowing on the film thickness and construct different waveguide structures by varying the index of the substrate and the surrounding medium. The results prove that feedback by waveguiding indeed plays an important role in the observed lasing behavior in this class of materials.

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. The film thicknesses used ranged from 27-252 nm for BuEH-PPV, 160-650 nm for BCHA-PPV and 52-405 nm for MEH-PPV. To demonstrate the effects of thickness on lasing behavior, we plot the high energy ($\geq 10 \mu\text{J}$) PL line width as a function of the film thickness for these three polymers in Figure 4. A well defined cutoff thickness for the presence of gain narrowing is evident around $116 \pm 10 \text{ nm}$ for BuEH-PPV, $215 \pm 30 \text{ nm}$ for BCHA-PPV and $70 \pm 15 \text{ nm}$ for MEH-PPV (see also Table 1).

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 which the fundamental mode cannot propagate.[20] This cutoff thickness is given by the following expression:

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

where λ 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.

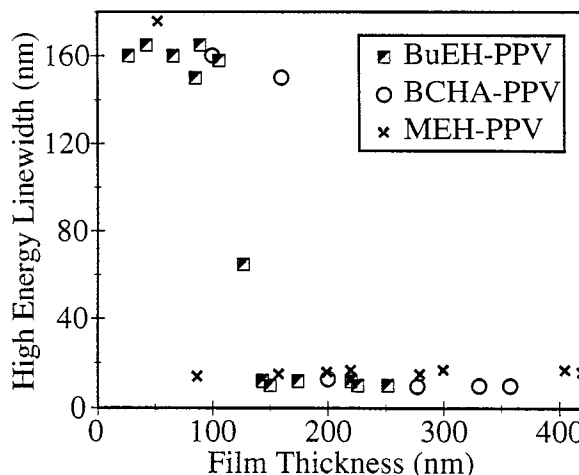


Fig. 4: High energy ($\geq 10 \mu\text{J}$) PL line width versus film thickness for BuEH-PPV, BCHA-PPV and MEH-PPV polymer thin films spin cast from THF on to glass substrates.

The refractive indices of BuEH-PPV and BCHA-PPV films were determined from modal waveguide characterization at 633 nm.[20] We note that the films exhibit birefringence: the refractive index in the plane of the film, determined from the angular position of the TE modes, was $n = 1.69$ for BuEH-PPV and $n = 1.60$ for BCHA-PPV, while the refractive index in the direction perpendicular to the plane of the film, determined from the angular position of the TM modes, was measured as $n = 1.55$ for BuEH-PPV and $n = 1.53$ for BCHA-PPV (the case of MEH-PPV is discussed below). Using the in-plane values of n in Eq. 1, the calculated h_{cutoff} values are 120 nm and 200 nm for BuEH-PPV and BCHA-PPV films on glass, respectively. Thus, for both BuEH-PPV and BCHA-PPV, the experimentally observed cut-off thicknesses are in excellent agreement with the values calculated from the asymmetric waveguide cut-off formula, Eq. 1. We also note that the observed cutoff thickness for the DCM/PS films lead to a calculated n between 1.56 and 1.59 (Table 1), in excellent agreement with handbook values for the index of refraction of pure PS.

The variation in the experimental cutoff thicknesses with polymer (Fig. 4) arises from differences in the polymer refractive indices. The larger the refractive index of a polymer film, the lower the cutoff film thickness for the observation of gain narrowing. The close correspondence of experimental and calculated cutoff thicknesses for the propagation of the fundamental mode in BCHA-PPV and BuEH-PPV offers a method for determining the refractive index for those materials where waveguide characterization cannot be used. For MEH-PPV, we calculated the refractive index of the film to be in the range $1.8 \leq n_f \leq 2.0$ from Eq. 1 based on the experimentally measured cutoff thickness. This is consistent with the fact that the light could not be coupled into the MEH-PPV film in the waveguide characterization experiment since the refractive index of the prism coupler ($n \sim 1.8$) is comparable to or lower than that of the film. This relatively high calculated value of the index for MEH-PPV is also consistent with other reports in the literature.

We have performed additional experiments to explore the role of waveguiding in lasing conjugated polymers. First, a BuEH-PPV/glass sample which was too thin (43 nm) to show line narrowing as an asymmetric waveguide in air was immersed in a solvent that was approximately index matched to the glass substrate (cyclohexanone, $n = 1.49$) and did not dissolve the polymer. This produced a configuration with a symmetric

waveguide structure (glass/polymer/solvent), where no minimum film thickness for waveguiding is expected.[20] Once in the solvent, the film showed dramatic line narrowing. This process is reversible: removing the film from the index matched solvent causes the laser behavior to disappear. This observation eliminates other explanations for the thickness dependence of the gain narrowing, such as loss of optical density as the film thickness decreases. This result also proves that the thin film waveguide structure is critical to the production of lasing in these films, and eliminates the possibility of purely superradiant emission in the absence of "optical feedback".

In a second set of experiments, we altered the waveguide structure by choosing a different substrate, casting BuEH-PPV films ($n = 1.69$) on to optically flat sapphire ($n = 1.76$). The PL spectrum recorded in the standard configuration (pumping directly into the film) showed only limited gain narrowing with a high threshold. However, exciting the film through the sapphire substrate produced strong gain narrowing. This observation can be explained in terms of waveguiding in the substrate. Since the refractive index of the substrate is higher than that of the film, some of the emitted light that travels into the substrate will be guided by multiple reflections in the substrate. However, the evanescent wave that penetrates from the substrate into the excited film can be amplified. Pumping from the top of the optically thick film does not sufficiently excite the polymer near the substrate interface where the guided evanescent wave penetrates; pumping through the substrate is an ideal configuration. To confirm this hypothesis, a BuEH-PPV/sapphire film that showed gain narrowing with a low threshold when pumped through the substrate was immersed in a high-index solvent, diiodomethane ($n = 1.75$). Since this solvent is approximately index matched to sapphire, the waveguiding effect is expected to disappear. Regardless of the pumping geometry, the gain narrowing was in fact completely inhibited when this sample was immersed in the high index solvent. These results are also consistent with previous work on dye doped sol-gel composites, where laser operation in thin films was observed to result from a similar substrate waveguiding mechanism.[22]

Whether waveguiding takes place in the polymer film or in the substrate, it seems surprising, at first, that there is little angular dependence to the gain narrowing. Since the guided light is nominally confined to the plane of the sample, one might expect to observe gain narrowing only in the plane of the sample. The glass substrates used, however, are not optically flat. Moreover, even on optically flat sapphire substrates, the thickness of the spincast polymer film typically varies by ~10%. These irregularities in the sample and substrate surfaces lead to imperfections in the natural waveguide which allow light to escape. Thus, guided light scatters in directions closer to the sample normal due to waveguide losses. This picture provides a rationalization for the observation of essentially isotropic nature of the gain narrowed spectrum in the thin film polymer samples.

Thus, we have demonstrated that waveguiding is responsible for photon confinement and plays a crucial role in gain narrowing in thin films of photoluminescent conjugated polymers. Gain narrowing was observed for both low and high refractive index substrates: For the former (glass), waveguiding occurs in the bulk of the polymer film, whereas for the latter (sapphire), photon confinement takes place in the substrate and gain narrowing occurs only when the region near the polymer/substrate interface is sufficiently excited.

5. The Role of Polymer Chain Packing in Laser Action

The interactions between polymer chains in neat films can profoundly affect the luminescence characteristics. One manifestation of this should be a dependence of the PL on the

morphology of the polymer chains in the film: interchain interactions are a strong function of the chain packing. In this section, we present an initial investigation into the role of morphology and chain conformation on the gain narrowing of neat conjugated polymer films by considering the influence of the solvent from which the films were cast.

Initially, we studied the effect of spin-casting solvent on lasing for BuEH-PPV films. The lasing characterization experiments showed similar threshold energies for gain narrowing and similar final line widths, independent of the solvent (THF or *p*-xylene) from which the films were cast (Table 1). However, somewhat different cutoff thicknesses for lasing were determined for films cast from each solvent, indicating that the in-plane refractive index of the film depends on the type of solvent used in the spin casting process. This is clearly a result of changes in polymer chain conformation and morphology with casting solvent.

The solvent dependence of the gain narrowing for cast films of MEH-PPV, in contrast, is quite pronounced. Fig. 5a illustrates the PL spectra under strong pumping conditions (~10 μ J) for films spin cast from different solvents. The films cast from THF show a narrow final line width (17 nm), in contrast with the broad final widths (≥ 50 nm) obtained from films cast from chlorobenzene (CB) or *p*-xylene, even under strong pumping conditions. Fig 5b shows the evolution of line width as a function of pump energy (cf. Figure 2). In addition to the increase in final line width, it is clear that the threshold for the limited line narrowing that takes place in MEH-PPV films cast from the aromatic solvents is more than five times higher than for

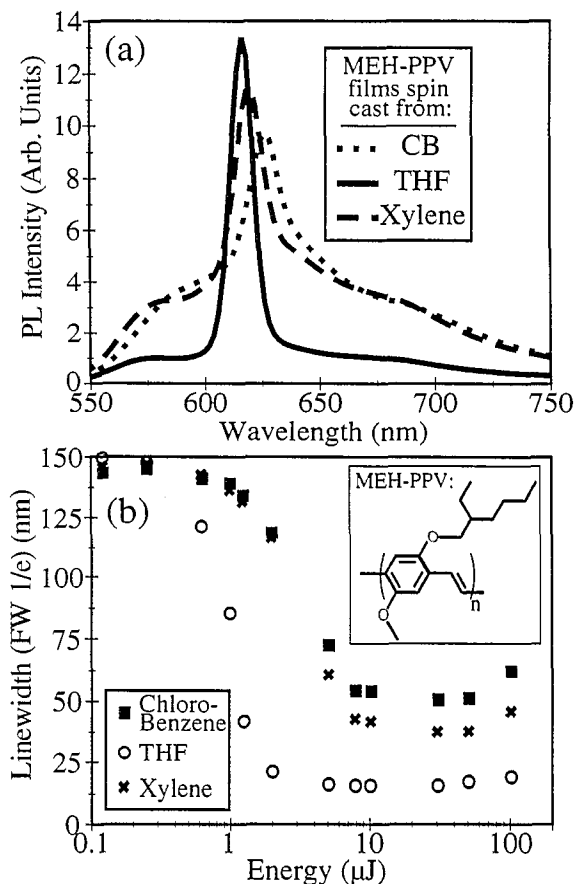


Fig. 5: (a) PL spectra at high pump energy ($\geq 10 \mu$ J) for neat films of MEH-PPV spin cast from different solvents. (b) PL line width vs. pump energy for the same films as (a); structure of MEH-PPV.

films cast from THF (see also Table 1).

These results are especially interesting in the context of previous ultrafast spectroscopic data that showed no SE from neat films of MEH-PPV cast from CB.[14] THF provides a much different chemical environment from the aromatic solvents, as evidenced by a blue-shift of the absorption of dilute MEH-PPV/THF solutions compared to solutions of MEH-PPV in CB or *p*-xylene. Here, we offer one argument to suggest that the difference in gain narrowing behavior may be partly the result of differences in π - π interactions between the conjugated polymer and the different solvents. Because the polymer chains are more rigid in the aromatic solvents, they likely lay down with a large degree of π interaction between them when the film is spin-cast, an effect which may be enhanced by the slow evaporation of these high-boiling solvents. THF, on the other hand, is low-boiling but fairly polar solvent. It is likely that the non-polar polymer chains are more kinked in these polar solutions (the absorption blue shift in THF likely reflects decreased conjugation length due to twisting), so the rapid evaporation of the solvent upon casting may lead to quick formation of a highly amorphous film with little time for development of π - π interchain interactions. This argument provides a rationalization for how changes in chain packing with casting solvent may be manifest, for example, in a reduction in interchain excited state absorption that may improve the SE or by changes in refractive index. Of course, there is also a dependence on the overall film quality and morphology with spin casting solvent which might affect the quality of the thin film waveguide structures. Therefore, choice of the proper solvent may offer an alternative way to control or enhance laser action. Further research in this area toward a better understanding of this effect is currently in progress and will be reported in due course.

6. Conclusions and Future Directions

In summary, we have demonstrated that conjugated polymers form a new class of solid-state laser materials, with laser emissions that span the visible spectrum (Table 1). Because of their strong absorption coefficients, the high density of chromophores and the Stokes-shifted luminescence, luminescent conjugated polymers have potential as laser media with extremely low thresholds, even in submicron thick films. The novelty of these materials was demonstrated in dilution studies, which show a highly non-linear dependence of the threshold for gain narrowing on polymer concentration indicative of coherent emission. Moreover, films of semiconducting polymers show a lasing threshold which is over 3 orders of magnitude lower than comparable solid films containing conventional laser dye. By changing substrates and using index matched solvents, we demonstrated that the thin films constitute simple waveguide structures and that channeling of the emitted light is an important ingredient in controlling the gain narrowing of these materials. Changes in chain conformation and film morphology, brought about by varying the solvent from which the polymers are cast, also have marked effects on the index of refraction and lasing properties of conjugated polymers.

The observation of lasing in optically pumped neat films of a class of conjugated polymers with the aid of only a simple waveguiding mechanism offers the promise of constructing electrically pumped solid state diode lasers with such polymers as the active gain medium. There are three major hurdles that must be overcome before this promise can be fulfilled. First, carrier concentrations sufficient to produce laser action must be demonstrated by electrical pumping. Current densities of 25 A/cm² have been reported in electrically pulsed MEH-PPV diodes (4x10⁻³ cm² area) when operated with 3 μ s pulses at low

duty cycle.[23] Based on the photon densities with the ~10 ns pulses in the present optically pumped study and assuming an internal quantum efficiency for electroluminescence of a few percent, the transient current densities necessary to reach the threshold for gain narrowing may be in excess of a few hundred A/cm². Construction of the laser diode with a high-Q resonant cavity or improved waveguiding structure instead of the rudimentary waveguides described here should provide a further decrease in the threshold for lasing. Therefore, with small active areas, low duty cycles, and good thermal management, sufficiently high current densities should be accessible.

Second, the solid-state polymers that have been studied to date have short SE times which are limited by an interfering excited state absorption. While this is not a difficulty for demonstrating optically pumped polymer lasers since gain takes place before the absorption relaxes to mask the SE, this might not be the case for injected carriers in an electrically pumped device. If such carriers have the same interchain excited state absorption as in the optically pumped samples, the induced absorption could overwhelm the SE. This problem can be overcome, however, by using a material in which the excited state absorption never interferes with the SE. We are presently surveying for such suitable materials, the signature of which is an SE decay time that persists for the entire lifetime of the PL.

The third and perhaps greatest challenge lies in the need to have carrier injecting electrodes, such as indium tin oxide (ITO) or metals, in direct contact with the conjugated polymer. According to our preliminary findings, the presence of high index ITO ($n > 2$) or metals such as gold in contact with the polymer has a detrimental effect on the optically induced lasing behavior, presumably because of the crucial role played by waveguiding. Since recombination in polymer diodes does not generally take place near the ITO interface, the evanescent wave from light guided in the ITO electrode will not undergo amplification. It is also possible that the presence of metal in close proximity quenches the luminescence, as evidenced by lower absolute PL quantum yields for polymers on ITO compared to glass.[24] Developing a carrier injecting mechanism that does not hamper the waveguiding effect or lower the overall Q of a microcavity therefore remains an important task in the development of polymer laser diodes.

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References:

- (1) Tomozawa; H.; Braun, D.; Heeger, A. J. *Synth. Met.* **1987**, *22*, 63.
- (2) (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.
- (3) (a) Yu, G.; Heeger, A. J. *J. Appl. Phys.* **1995**, *78*, 4510. (b) Halls, J. J. M.; Walsh, C. A.; Greenham, N. C.; Marseglia, E. A.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Nature* **1995**, *376*, 498.
- (4) Yang, Y.; Heeger, A. J. *Nature* **1994**, *372*, 344.
- (5) (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.
(c) Cao, Y.; Yu, G.; Heeger, A. J.; Yang, C. Y. *Appl. Phys. Lett.* **1996**, *68*, 3218.
- (6) (a) Cimrová, V.; Neher, D. *J. Appl. Phys.* **1996**, *79*, 3299. (b) Berggren, M.; Inganäs, O.; Granlund, T.; Guo, S.; Gustafsson, G.; Andersson, M. R. *Synth. Met.* **1996**, *76*, 121. (c) Lidzey, D. G.; Weaver, M. S.; Fisher, T. A.; Pate, M. A.; Whittaker, D. M.; Skolnick, M. S.; Bradley, D. D. C. *Synth. Met.* **1996**, *76*, 129. (d) Grüner, J.; Cacialli, F.; Samuel, I. D. W.; Friend, R. H. *Synth. Met.* **1996**, *76*, 137. (e) Fisher, T. A.; Lidzey, D. G.; Pate, M. A.; Weaver, M. S.; Whittaker, D. M.; Skolnick, M. S.; Bradley, D. D. C. *Appl. Phys. Lett.* **1995**, *67*, 1355. (f) Wittman, H. F.; Grüner, J.; Friend, R. H.; Spencer, G. W. C.; Moratti, S. C.; Holmes, A. B. *Adv. Mater.* **1995**, *7*, 541 (1995).
- (7) (a) Hide, F.; Schwartz, B. J.; Díaz-García, M. A.; Heeger, A. J. *Chem. Phys. Lett.* **1996**, *256*, 424. (b) Schwartz, B. J.; Hide, F.; Díaz-García, M. A.; Andersson, M. R.; Heeger, A. J. *Electronics with Molecular Materials: From Synthesis to Device*, in Proc. Royal Soc. Disc. Meeting, **1996**, Proc. Roy. Soc. in press.
- (8) (a) Hide, F.; Díaz-García, M. A.; Schwartz, B. J.; Andersson, M. R.; Pei, Q.; Heeger, A. J. *Science*, in press. (b) Díaz-García, M. A.; Hide, F.; Schwartz, B. J.; Heeger, A. J. *U. S. Patent* (submitted). (c) Schwartz, B. J.; Díaz-García, M. A.; Hide, F.; Andersson, M. R.; Pei, Q.; Heeger, A. J. *J. Am. Chem. Soc.* (submitted).
- (9) Zhang, C.; Höger, S.; Pakbaz, K.; Wudl, F.; Heeger, A. J. *J. Electron. Mater.* **1993**, *22*, 413.
- (10) Gettinger, C. L.; Heeger, A. J.; Drake, J. M.; Pine, D. J. *J. Chem. Phys.* **1994**, *101*, 1673.
- (11) Yang, Y.; Pei, Q.; Heeger, A. J. *J. Appl. Phys.* **1996**, *79*, 934.
- (12) (a) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416. (b) For past polyfluorene work, see Ohmori, Y.; Uchida, M.; Morishima, C.; Fujii, A.; Yoshino, K. *Jpn. J. Appl. Phys.* **1993**, *32*, L1663.
- (13) (a) Moses, D. *Appl. Phys. Lett.* **1992**, *60*, 3215. (b) Holzer, W.; Penzkofer, A.; Gong, S.-H.; Bleyer, A.; Bradley, D. D. C. *Adv. Mater.*, in press. (c) Brouwer, H.-J.; Krasnikov, V. V.; Hilverer, A.; Wildeman, J.; Hadziioannou, G. *Appl. Phys. Lett.* **1995**, *66*, 3404.
- (14) Yan, M.; Rothberg, L.; Kwock, E. W.; Miller, T. M. *Phys. Rev. Lett.* **1995**, *75*, 1992.
- (15) (a) Yan, M.; Rothberg, L. J.; Papadimitrakopoulos, F.; Gavin, M. E.; Miller, T. M. *Phys. Rev. Lett.* **1994**, *72*, 1104. (b) Kersting, R.; Lemmer, U.; Mahrt, R. F.; Leo, K.; Kurz, H.; Bäessler, H.; Göbel, E. O. *Phys. Rev. Lett.* **1993**, *70*, 3820. (c) Graupner, W.; Leising, G.; Lanzani, G.; Nisoli, M.; DeSilvestri, S.; Scherf, U. *Phys. Rev. Lett.* **1996**, *76*, 847. (d) Pauck, T.; Hennig, R.; Perner, M.; Lemmer, U.; Siegner, U.; Mahrt, R. F.; Scherf, U.; Müllen, K.; Bäessler, H.; Göbel, E. O. *Chem. Phys. Lett.* **1995**, *244*, 171.
- (16) (a) Schwartz, B. J.; Hide, F.; Andersson, M. R.; Heeger, A. J. *Chem. Phys. Lett.*, submitted.
- (17) Yariv, A. *Quantum Electronics*, 3rd. edn.: Wiley, New York, **1989**.
- (18) Heeger, A. J.; Kivelson, S.; Su, W.-P. *Rev. Mod. Phys.* **1988**, *60*, 781.
- (19) Hammond, P. R., *Opt. Commun.* **1979**, *29*, 331.
- (20) Kogelnik, H. in *Topics in Applied Optics: Integrated Optics*, T. Tamir, Ed., Springer-Verlag, Berlin, **1979**; Chapter 2.
- (21) We have chosen the full width at $1/e$ height to represent the line width of the emission spectra since this is more suitable (compared to other definitions such as FWHM) for comparison of disparate emission spectra with varying magnitudes of vibronic features.
- (22) Shamrakov, D.; Reisfeld, R. *Chem. Phys. Lett.* **1993**, *213*, 47.
- (23) Braun, D.; Moses, D.; Zhang, C.; Heeger, A. J. *Appl. Phys. Lett.* **1992**, *61*, 3902.
- (24) Greenham, N. C.; Samuel, I. D. W.; Hayes, G. R.; Phillips, R. T.; Kessener, Y. A. R.; Moratti, S. C.; Holmes, A. B.; Friend, R. H. *Chem. Phys. Lett.* **1995**, *241*, 89.